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Abstract (200 words)

The Center for Atomic Clusters-derived Materials performed a broad range of research concerned with synthesizing, characterizing and utilizing atomic and molecular clusters, nanoparticles and nanomaterials. Our most important result was the development of a nanoparticle-based technology for DNA detection that has now been commercialized, and which holds the promise of revolutionizing this field. A second important result was the development of a method for chemical and biological agent detection based on localized surface plasmon absorption. Other projects included the structural characterization of atomic clusters of all of the group 14 elements, important developments in carbon nanotube conductivity and mechanical properties, advances in optical property theory, electronic conductivity theory and the theory of DNA melting, new methods of synthesis of metal nanoparticles and nanoparticles that are coated with organics and/or DNA, the first observation of nonlinear optical properties such as hyperRayleigh scattering for nanoparticles, and the synthesis and characterization of new classes of magnetic nanoparticles. Fourteen students received Ph.D. degrees, and most are now employed in industry.

(1) Foreword

This Final Progress Report describes research and other activities associated with the Center for Atomic Cluster-derived Materials. This multifaceted center was aimed at pushing back the frontiers in the rapidly developing areas of nanotechnology that relate to nanoparticles, including such diverse applications as chemical and biological sensing, optical communications, molecule based electronics, infrared detection and advanced magnets. One successful spin-off from this program was a technology for DNA detection that led to the formation of the company Nanosphere, Inc. This company has gone through three rounds of funding, and its first generation of products are about to be released. Important interactions and collaborations with DoD personnel were established during the grant, and many of these continue to function now that the grant is over. Many collaborations between MURI supported research groups were initiated during this grant, including several joint students and postdocs. Fourteen students received Ph.D. degrees, and most are now employed in industry.

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(3) List of Appendices:

1. Technology Transfer
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(4) Statement of the problem studied

This project was concerned with making and characterizing atomic and molecular clusters and nanoparticles, and exploring their use in such applications as chemical and biological sensing, infrared detection, electrical, photonic and optoelectronic devices, and nonvolatile magnetic memories. We did a very large amount of work with silver and gold nanoparticles, as these can be made in many different ways, they have unique optical, chemical and electrical properties, and it is possible to take advantage of these properties to develop sensors, and devices. Included in these studies were new approaches to chemically functionalize nanoparticles, methods for making nanoparticles that have controlled sizes, shapes and arrangements, so that their optical and electrical properties may be carefully tuned, and new methods for combining nanoparticles with optical components so that the interaction of light with nanoparticles can be manipulated. We studied carbon clusters (fullerenes and nanotubes) very extensively, and silicon, hydrogen terminated silicon, germanium, tin and lead clusters in less detail, in all cases with the goal of determining their structural and optical properties, and how their structural and optical properties change with particle size. For carbon nanotubes we discovered exciting electrical and mechanical properties that suggest that important breakthrough technologies may be made from them in the future. We also studied magnetic nanoparticles with the goal of determining if their structural and magnetic properties are correlated. Integrated throughout these projects were theoretical studies of cluster nanoparticle structural, optical, electrical and magnetic properties.

(5) Summary of the most important results

Executive Summary (for the full 5 year period)

The project was divided into four thrust areas: (1) Aggregation-based biological sensors, (2) Group 4 cluster materials, (3) Nanoparticle chemical sensors and optical materials, and (4) Magnetic Nanoparticles.

(1) Aggregation-based biological sensors. The primary result of our work in this field was the development of a nanoparticle-based technology for DNA detection that has now been commercialized, and which holds the promise of revolutionizing this field. This was based on using DNA to trigger the aggregation of gold nanoparticles, leading to a color change that is easily detected by absorption or scattering, and electrical detection was also demonstrated. In addition to gold nanoparticles, silver particles coated by a gold shell were developed for this approach, providing multiplexing capabilities. Applications to the detection of anthrax, tularensis and other pathogens was demonstrated, including field tests at Dugway. We also demonstrated the use of this approach for detection of nucleoside polymorphisms in sickle cell anemia. Theory was used to guide and interpret these experiments, including electrodynamics theory for optical properties, electrical transport theory for conductivity measurements, and thermodynamics and molecular dynamics for DNA melting modeling.

(2) Group 4 cluster materials. In this area we used ion-mobility measurements to study the properties of carbon, silicon, germanium, tin and lead clusters with up to 100 atoms, and we studied hydrogen terminated silicon clusters as a model for the properties of porous silicon. In addition we performed surface enhanced Raman studies of certain of the carbon and silicon cluster ions, and from this we were able to determine important features of ion structures. A spin-off of this research

program was the study of carbon nanotube electrical and mechanical properties, including the demonstration that carbon nanotubes exhibit a ballistic conduction mechanism, and the use of nanotubes to weigh biomolecules.

(3) *Nanoparticle chemical sensors and optical materials.* This area emphasized studies of localized surface plasmon resonances (LSPR's) in silver and gold nanoparticles, including their use in chemical and biological sensing, and in nonlinear optical applications. Some of the metal nanoparticles were made using nanosphere lithography which is a relatively simple method for making arrays of nanoparticles of variable size and shape, which therefore allows one to tune the LSPR wavelength over a wide range (from the infrared to the near UV for the case of silver particles). To develop sensors based on LSPR's, we learned how to coat metal nanoparticles with self assembled monolayers (SAM's), and then to chemically functionalize the SAM's with receptor sites for binding proteins and other molecules. With that capability we demonstrated that it was possible to detect 100 protein molecules per nanoparticle, and at the end of the grant we demonstrated that it was possible to detect single nanoparticles, all using cheap components and extinction or scattering spectroscopy. In addition, we used the knowledge learned from the extinction spectra of metal nanoparticles to develop new approaches for doing surface enhanced Raman spectroscopy (SERS), and just at the end of the project we developed a new class of glucose sensor based on SERS that shows good promise for commercialization. Another modality for sensing that we developed involves HyperRayleigh spectroscopy (HRS) in combination with colloidal silver, copper and gold. This turns out to have surprisingly high intensities despite the nominal forbidden nature of HRS for spherically symmetric particles. In fact we demonstrated that HRS can be plasmon enhanced by both dipolar and quadrupolar plasmons. In both our linear and nonlinear spectroscopy studies, we used theory (classical electrodynamics) quite successfully to model plasmon excitation, taking advantage of recent advances in computational electrodynamics software that allows one to calculate extinction spectra for nanoparticles of arbitrary shape provided that the particles are less than 100 nm in each dimension. In addition, we have successfully developed new electronic structure methods for describing reverse saturable absorbers and two-photon absorption, and we have recently constructed a high speed switch by temporarily writing a grating in a film having a large nonlinear $\chi^{(2)}$ response.

(4) *Magnetic Nanoparticles.* In this area we studied two approaches to the synthesis and characterization of magnetic nanoparticles, lithography and molecular beams. Our molecular beam experiments have demonstrated that odd-numbered niobium clusters are diamagnetic. Also, we found that Co_5 is the smallest ferromagnetic Co cluster. We used both e-beam lithography and nanosphere lithography to make magnetic nanoparticles of Ni, Nb and Co. The dots were characterized using magnetic force microscopy and other techniques, and the magnetic transport properties were studied using ferromagnetic resonance.

Information about Specific Thrust Areas

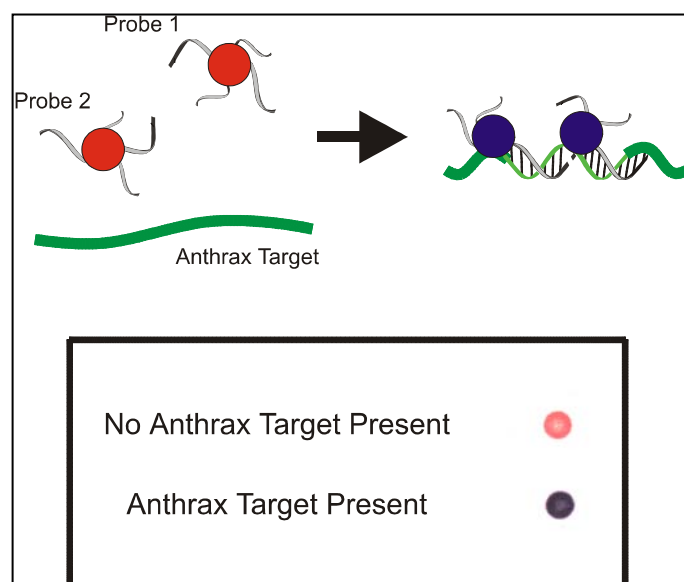
A. Aggregation-based biological sensors (Mirkin, Schatz, Ratner)

1. Introduction

This group was concerned with the fabrication of chemical sensors that combine the organism-specific binding capabilities of DNA together with aggregation-specific optical properties of metal nanoparticles. The research program included synthesis (oligonucleotides and nanoparticles), biodetection studies, spectroscopic characterization of nanoparticle aggregates, and theoretical studies of structural and optical properties.

2. DNA/gold particle biosensor studies

We developed a colorimetric nanoparticle based assay for anthrax and other pathogens. This was a major advance in that we can now work with double stranded DNA and there is at least the possibility that in certain kinds of studies we will have sufficient sensitivity to avoid PCR amplification. The work is being commercialized by Nanosphere, Inc, and there has been significant interaction with scientists at ARL labs, including tests at Dugway.



In the anthrax experiment, which is schematically illustrated in Figure 1, a 30 nucleotide region of a 141 mer anthrax PCR product (protective antigen portion) was detected using a dual probe oligonucleotide modified gold nanoparticle assay. Control experiments using only one probe, or a PCR product that is non-complementary to both the probes did not produce the blue spot that is indicative of nanoparticle aggregation by oligonucleotide hybridization. Importantly, the test is not disrupted by the PCR buffer mixture, which facilitates the ease and speed of the method.

Figure 1 Spot test results for anthrax detection using oligonucleotide modified gold nanoparticle

In related work we developed an approach for replacing the gold nanoparticles by gold coated silver particles such that the optical properties of the particles are those of silver while the chemical properties are those of gold. As a result, this test gives the has the same aggregation properties and DNA sensitivity as the gold test, but the color change is from yellow to brown when aggregation occurs rather than from red to blue. In addition, we demonstrated that it is possible to do the gold and silver nanoparticle tests on the same samples due to the different optical properties of the gold and silver particles, providing multiplexing capabilities for DNA detection.

In another project, we designed and implemented a fluorimetric assay for determining the average number of oligonucleotides attached to each Au particle and the hybridization efficiencies for the particles. A 13 nm particle can support approximately 210 oligonucleotides with approximately 1/3 available for hybridization. This assay allows us to optimize detection methods based upon oligonucleotide-modified nanoparticles; with it, we monitored surface loading and hybridization as a function of various environmental parameters (pH, salt concentration, oligonucleotide concentration, etc.). Finally, we have successfully extended this oligonucleotide-nanoparticle surface chemistry to CdS and CdSe quantum dots. Because of their novel optical properties, these types of particles open up a variety of avenues to new sensing modalities for DNA.

3. Electrodynamics of Nanoparticle Arrays and Aggregates.

An important challenge that we faced at the beginning of the MURI project was to understand the optical properties of aggregates of gold particles that are produced when DNA

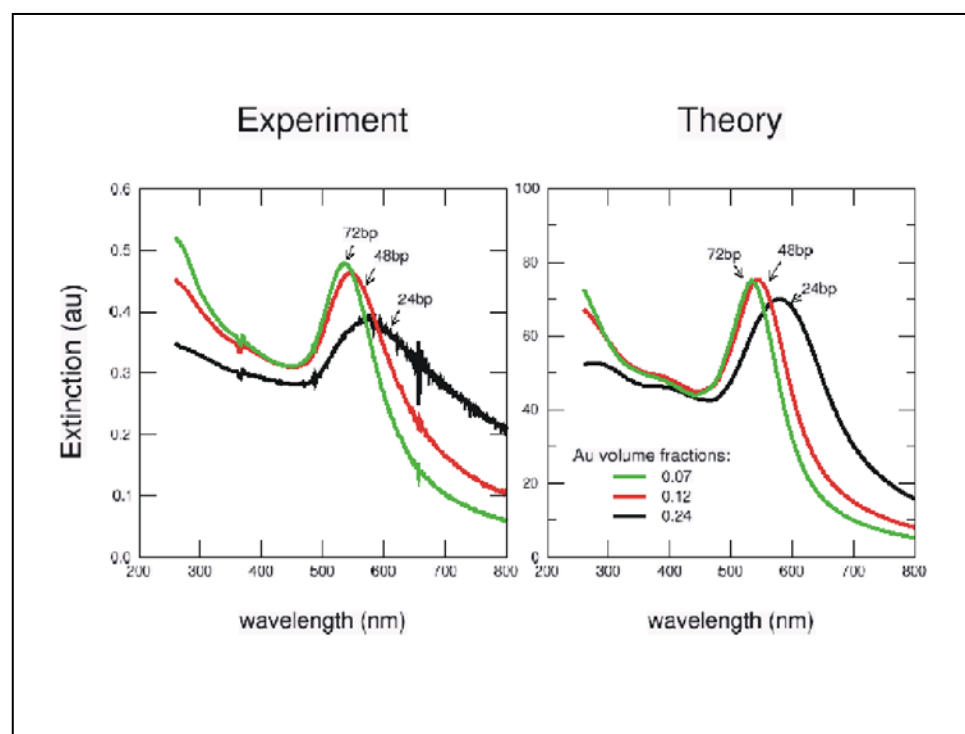


Figure 2. Extinction spectrum of nanoparticle aggregates, comparing experimental results with theory for three different linker lengths.

including:

- a. *finite element methods*, such as the Discrete Dipole Approximation (DDA), that are capable of a quantitative description of aggregate spectra for arbitrary configurations of the particles,
- b. *coupled dipole and multipole theories* that provide accurate descriptions of aggregates provided that the particles are not too close,
- c. *dynamic effective medium approximations* that represent the aggregate in terms of an average dielectric constant.

hybridization links the particles together, causing them to aggregate. What was observed was the transition from the red color of dispersed gold colloid to the blue color of the aggregate. This corresponded to a change in the plasmon resonance spectrum from a peak at 520 nm to a red-shifted peak at 580 nm that was also greatly broadened.

We studied this problem from many different perspectives,

Using these theories, we demonstrated that for typical DNA-linked aggregates produced in the Mirkin group biosensors, i.e., 24 bp duplexes linking 13 nm gold spherical particles, the particles are of sufficiently low density that either coupled dipole or effective medium approximations provide a quantitative description of the aggregate optical properties. The theory also indicates that the red to blue color change associated with the Mirkin DNA detection method is associated with

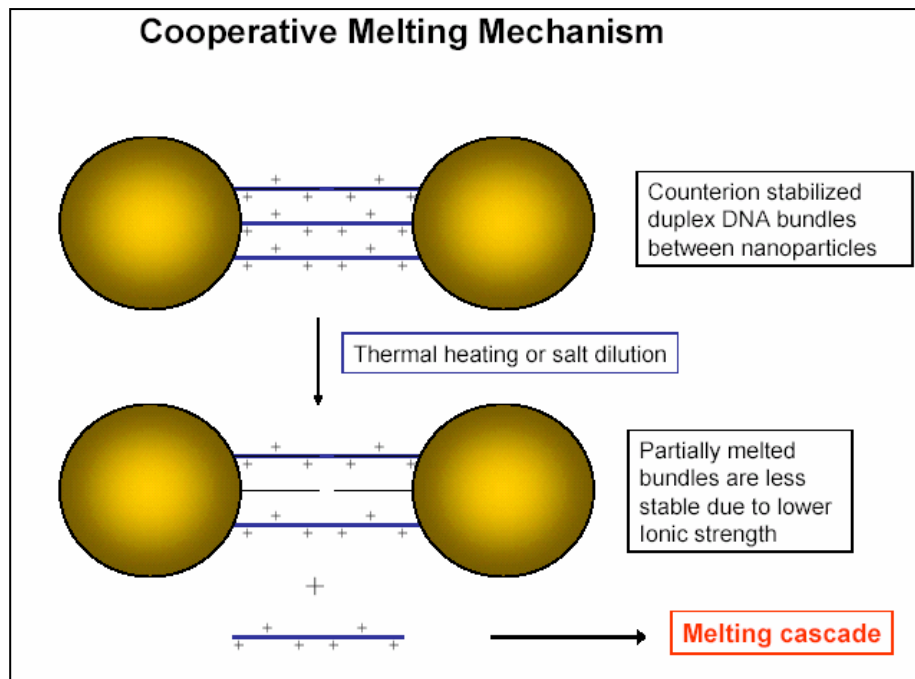


Figure 3. Schematic of cooperative melting mechanism, showing two gold particles linked by three DNA's. When the first DNA melts, it takes positively charged counterions into solution, leaving the aggregate depleted in counterions,

forming aggregates of thousands of gold particles, with dimensions in the hundreds of nanometers, that shift the plasmon resonance from the single particle peak at 520 nm to the aggregate peak at 580 nm. Figure 2 compares the calculated spectrum (based on effective medium theory, with the measured spectrum for three different linker lengths: 24, 48 and 72 base pairs. Note that the red shift associated with coupling between two particles is very small (few nm), however the collective response of

thousands of electromagnetically coupled particles is much larger (> 50 nm), and there is a substantial broadening of the plasmon resonance feature as well. Longer pieces of DNA, such as 48 or 72 bp duplexes, separates the particles by larger amounts, so there the red shifts are smaller. Smaller DNA produces even larger shifts, but DNA sensing may not be able to uniquely identify an organism for fewer than 20 base pairs. The theory also indicates that for aggregates that have several micron dimensions, the plasmon resonance moves back to near the single sphere resonance at 520 nm, and becomes independent of aggregate size.

4. Theory of DNA melting in gold nanoparticle aggregates.

A key property of the gold nanoparticle aggregates is their unexpectedly narrow melting transitions. DNA in solution undergoes a transition from hybridized to single-stranded form over a temperature range of about 20° at a melting temperature of typically 50°C . When the same DNA is used to link gold nanoparticles, making an aggregate of thousands of particles, the melting is found to narrow to 3° or less. The melting temperature is typically about the same, although one needs to be careful in stating this as the salt and DNA concentrations are typically quite different, and melting is sensitive to these properties.

To explain the narrow melting, we have developed a thermodynamic model that ascribes the

sharper transition as arising from two effects: multiple DNA's connecting between each pair of nanoparticles, and cooperative behavior in the melting equilibrium due to overlap of the ion clouds around each DNA.

Figure 4. The ion distribution (viewed down the helical axis) of two DNA duplexes separated by 3 nm

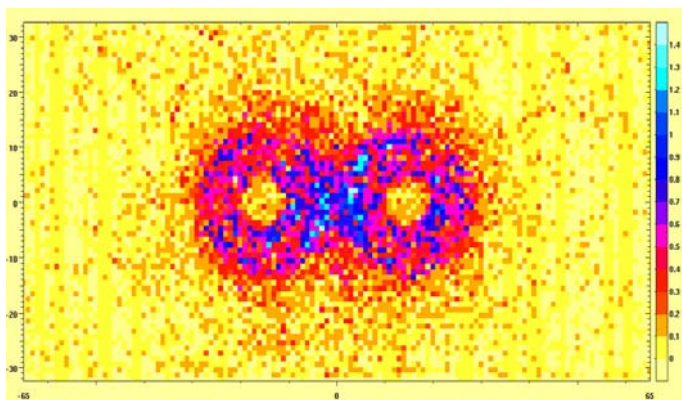


Figure 3 shows a schematic of this model. This model predicts that overlap of the ion atmospheres leads to stabilization of the duplex such that there is a higher melting temperature for the first step of melting than for subsequent steps, so as soon as the first DNA melts, all those nearby will also melt.

To confirm the underlying assumptions of the thermodynamic model, we have performed molecular dynamics studies of DNA dimers, Figure 4, to see if the overlap of the ion

atmospheres leads to mutual stabilization and an increase in the melting temperatures. Preliminary results indicate that for separations smaller than 4 nm, overlap of the ion-atmospheres is important enough to produce the assumed cooperative stabilization. We are now using the results from the MD calculations to refine the thermodynamic model so that structural information about the aggregate can be included.

5. Electron Transport Theory in Cluster-derived Materials.

The general subject of molecular electronics is an important one (*Science* magazine called it the breakthrough in the year 2001). Here the cluster aspect enters at the interface - the molecule interacts with the cluster of local metal atoms, which in turn extend to the bulk. In addition, the gold nanoparticle/DNA aggregates noted above may constitute the current carrying element, in which case the metal clusters, or particles, are components of the circuit.

We have developed a nonequilibrium Green's function formalism for treating electrical transport in these and other problems generally, and have applied it to such issues as optimized electron injection at interfaces, analysis of the voltage dependence of the electrostatic potential across molecules, the nature of binding at the interface and how it effects molecular currents, the difference between semiconductor and metal electrodes (particular attention paid to injection from nanoscale titania into a metallic surface), analysis of the so-called band lineup between the molecular levels and the Fermi levels of the metal. We have also completed a series of investigations into the role of image charges in stabilizing and modulating the injection process. Finally, we have begun a collaboration with the Naval Research Laboratory studying molecular currents in a crossed wire geometry.

In all, the research in the group has been devoted to understanding how simple molecular concepts need to be extended to deal with several interacting molecules (intermolecular cluster) or when the molecule abuts the metal semiconductor electrode (interaction of molecule with a cluster assembled species). We feel that, through collaboration with our partners in the MURI Grant, we

have learned a substantial amount both about organic-based cluster systems and about appropriate formalisms for dealing with the complicated metal/molecule interaction problem.

B. Group 4 cluster materials (de Heer, Jarrold, Ratner, van Duyne)

1. Introduction

This group was concerned with the development of new materials that can be made from atomic clusters of group 4 (carbon, silicon, germanium, tin and lead). The research program emphasized ion mobility measurements of cluster structure, Raman studies of cluster spectra, and carbon nanotube synthesis and mechanical and conductivity properties.

2. Structure and Optical Properties of Carbon Clusters. Using laser ablation in combination with ion mobility measurements, we were able to prepare carbon clusters C_n for n between 1 and several hundred. The mobility measurements indicated that carbon clusters can take on several structural forms, including stick-like linear structures, rings, sheets and fullerenes, depending on n . To better characterize some of the smaller structures, we obtained surface plasmon polariton (SPP)-enhanced Raman spectra of size-selected C_{16} , C_{18} , and C_{20} clusters isolated in nitrogen matrices along with the calculated vibrational frequencies for the ring and linear chain isomers. The Raman spectra, recorded at a range of excitation wavelengths from 457.9 to 670 nm, show strong resonance enhancement for the three clusters. Calculated vibrational frequencies from ab initio studies for ring and linear chain isomers and the cage and bowl structures for C_{20} , were compared to experimental frequencies, and systematic shifts in the series of peaks in the 200 cm^{-1} region for C_{16} , C_{18} , and C_{20} suggested that the observed isomers have the same geometry, thereby ruling out the bowl and cage isomers for C_{20} . The measured spectra appear to be most consistent with the linear chain isomer. This high energy isomer may have been produced from the C_{20} ring isomer during neutralization of the deposited cluster ions.

The surface plasmon polariton-enhanced Raman spectra of size-selected, matrix-isolated C_{14} neutral clusters were measured along with the calculated vibrational frequencies for the ring and linear chain isomers. The Raman spectra show resonance enhancement over a range of excitation wavelengths from 457.9 to 514.5 nm. The measured vibrational spectra are most consistent with the linear chain isomer. In addition, the first fluorescence spectra of neutral, mass-selected C_n (14, 18) clusters were measured. The isolated C_{14} clusters display strong fluorescence and vibronic structure between 520 and 700 nm. The origins of the observed fluorescence for both C_{14} and C_{18} (previously reported) were investigated using the ZINDO/S, CIS and TD-B3LYP methods.

We completed extensive studies of the structures of carbon, silicon, germanium, tin and lead clusters using ion mobility methods. As part of this work, we developed a new model to evaluate the gas phase mobility of an ion based on elastic scattering on an electronic density isosurface (SEDI). In this method the ion is represented by a surface of arbitrary shape defined as a set of points in space where the total electron density assumes a certain value. This value is the only adjustable parameter in the model. Conceptually, this treatment emulates the interaction between a drifting ion and the buffer gas atoms closer than the previously described methods, the exact hard spheres scattering (EHSS) model and trajectory calculations, where the scattering occurs in potentials centered on the nuclei. We employed EHSS, trajectory calculations, and SEDI to compute the room temperature mobilities for low energy isomers of Si_n ($n \leq 20$) cations and anions optimized by density functional theory (DFT) in the local density approximation and generalized gradient approximation. The results produced by SEDI were in excellent agreement with the measurements

for both charge states, while the other methods could fit the mobilities of the cations only. Using SEDI we confirmed the structural differences between Si_n^+ and Si_n^- predicted by DFT calculations, including the major structural rearrangements for $n = 9, 15, 16$, and 18 . We also assigned the multiple isomers observed in recent high resolution ion mobility measurements for Si_n^+ with $n = 17-19$, some of them to near-spherical cage-like geometries.

3. Structure of group 14 clusters

Our studies of the structures of silicon, germanium and tin clusters, using ion mobility measurements, have shown that in the intermediate size regime these clusters all adopt similar prolate geometries produced by stacking tricapped trigonal prism units. Small tin clusters have the same geometries that result from directional covalent bonding in silicon and germanium clusters. However, Pb_n cations up to $n = 32$ assume compact near-spherical morphologies for all sizes studied. This behavior is characteristic of clusters of the metallic elements. So the transition to “normal” metal cluster growth in the group 14 elements occurs between tin and lead, one row lower than the transition from covalent to metallic bonding in the bulk solids under ambient conditions.

Since the discovery that soccerball-like carbon molecules form upon vaporization of graphite, there has been a tremendous interest in the mechanism of this extraordinary process. How the self-assembly of specific, perfectly-symmetric fullerene cages occurs in substantial yield under the highly-entropic conditions of a hot carbon plasma has been regarded as a major puzzle. The earliest proposal, “The Pentagon Road” where fullerenes were envisioned to result from icospiral curling of graphite sheets, is now known to be flawed. The hypothesis that fullerenes grow in a carbon plasma by the addition of C_2 units (the “Fullerene Road”) has been widely acclaimed as the most plausible mechanism for formation of larger fullerenes including C_{60} and C_{70} . Calculations suggest that the association of C_2 with fullerenes proceeds through two classes of intermediates, “sticks” and “handles”. We have since identified new carbon cluster isomers that have mobilities expected for “stick” and “handle” geometries for C_n cations generated by laser vaporization of graphite and laser desorption of C_{60} . These species are almost certainly intermediates along the “Fullerene Road”. The observation that these intermediates are ubiquitous in a hot carbon plasma is strong support for this mechanism of fullerene growth.

3. Electron transport in carbon nanotubes (CNT)

The CNT project was a spin-off of our carbon cluster work, and it involved two important directions in carbon nanotube investigations. One involved a long-standing problem of measuring the conductivity of CNT's, where traditionally the quality of the contact was a determining factor. To overcome this problem, we succeeded in contacting a supported CNT with a liquid metal droplet, hence insuring two good contacts. The resistance of the nanotubes were found to be close to 13 k Ohm , irrespective of their lengths and diameters which indicates that the transport through these objects is ballistic (i.e. without electronic scattering). This ballistic transport behavior presents a striking contrast with more traditional molecular wires, and the Hg(liquid) interface used here avoids the injection limitations that normally is found at the metal/molecule interface.

The conductivity experiments were performed in absence of direct observation of the CNT which was conducting the current. Since this a shortcoming of the experiment, we therefore initiated a series of in-situ electron microscope experiments to directly observe the CNT's in the electron microscope with the possibility to manipulate them externally and to apply potentials to them. These

new experiments verified our original conclusions, shed further light on the previous experiments, while at the same time suggesting further in-situ experiments. In particular, we were able to induce high frequency mechanical resonances in the CNT's whereby we could accurately measure their mechanical properties. These results, which suggest a new approach towards nanomechanics, were published in Science (March 1999). Figure 5 shows the nanotubes with and without voltage applied, and it also shows the tip deflection as a function of voltage.

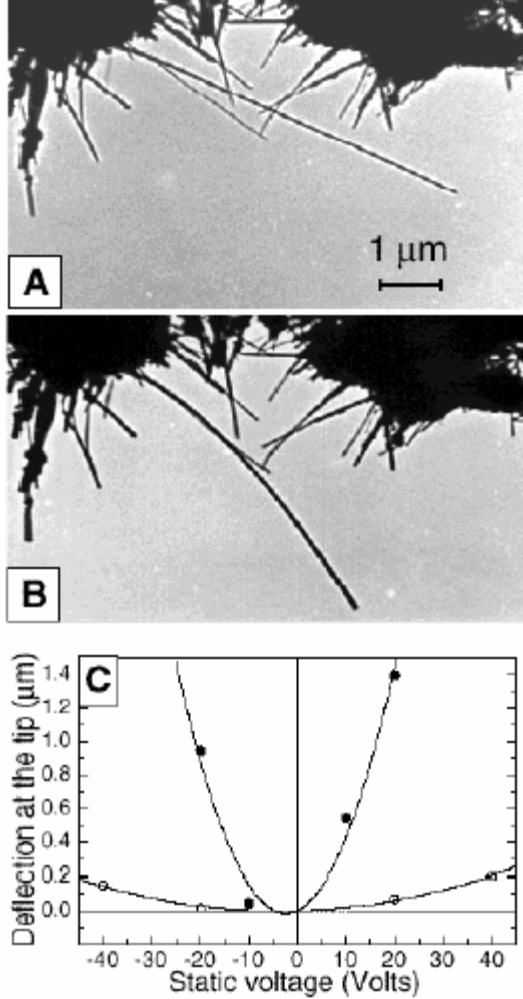


Figure. 5. Electron micrographs of the electro-mechanical deflections of a carbon nanotube. (A) Uncharged nanotube: $V_s=0$. (B) Charged nanotube: $V_s=20\text{V}$. Here an electrical potential difference is applied between the nanotube (which is connected to a nanotube fiber) and a counter electrode (not shown). The charge which is induced on the nanotube interacts with the electric fields between the nanotube and the counter electrode resulting in an attractive force which causes the nanotube to bend. An analysis of the shape of the bent nanotube shows that essentially all of the induced charge is at the tip of the nanotube. The bending process is reversible even for extreme bends (with radii of curvature $<100\text{ nm}$), which indicates the large elastic strength of the nanotubes. (C.) Measured static deflections as a function of V_s for two nanotubes (filled circles: $D=18\text{ nm}$, $L=4.6\ \mu\text{m}$; open circles: $D=41\text{ nm}$, $L=1.5\ \mu\text{m}$) showing the quadratic dependence on V_s . The slight voltage offsets of the minima of the fitted parabola are attributed to work function effects.

C. Nanoparticle chemical sensors and optical materials(Van Duyne, Hupp, Ketterson, Ratner, Schatz)

1. Introduction

The central goal of this group was to develop new types of atomic cluster based materials that have enhanced linear and nonlinear optical (NLO) properties. These materials have potential applications as chemical sensors, optical limiters, and as infrared detectors. To achieve this goal, we developed synthetic methods for preparing nanoparticles with controllable linear and nonlinear optical properties, and we performed spectroscopic studies (extinction, second harmonic generation, hyperRayleigh) of these particles in a variety of configurations and solvent environments. We also studied electrodynamics theory, including nonlinear electrodynamics, and molecular theories of nonlinear optical processes. Finally, we studied nonlinear optical cavities as a means for incorporating nanoparticle NLO materials into practical optical devices.

2. Nanosphere Lithography and LSPR spectroscopy.

Nanosphere lithography (NSL) is an inexpensive, simple to implement, inherently parallel, high throughput, materials general nanofabrication technique capable of producing an unexpectedly large variety of nanoparticle structures and well-ordered, 2D nanoparticle arrays. The scope of NSL was broadened considerably during the course of this grant to include strategies for the fabrication of several new nanoparticle structural motifs and their characterization by atomic force microscopy. Nanosphere lithography was also been demonstrated to be well-suited to the synthesis of size-tunable noble metal nanoparticles in the 20 - 1000 nm range. This characteristic of NSL has been especially valuable for investigating the fascinating richness of behavior manifested in size-dependent nanoparticle optics.

The use of localized surface plasmon resonance (LSPR) spectroscopy to probe the size-tunable optical properties of Ag nanoparticles and their sensitivity to the local, external dielectric environment (viz., the nanoenvironment) has been studied in detail. More specifically, the effects of nanoparticle size, shape, interparticle spacing, nanoparticle-substrate interaction, solvent, dielectric overlayers, and molecular adsorbates on the LSPR spectrum of Ag nanoparticles have been investigated. These fundamental studies in nanoparticle optics have resulted in a new class of chemical and biological nanosensors based on the shift in the LSPR wavelength maximum upon adsorption of the target analyte. The following systems have been characterized: (1) alkanethiol monolayers; (2) alkanethiol multilayers; (3) streptavidin/biotin; and (4) anti-biotin/biotin. LSPR nanosensing at the few hundred molecule per nanoparticle limit is a reality.

3. Surface-Enhanced Raman Spectroscopy and Sensing. The first systematic study of the surface-enhanced Raman scattering (SERS) properties of nanosphere lithography (NSL) derived Ag nanoparticles has been completed (C. L. Haynes and R. P. Van Duyne, *J. Phys. Chem. B*, submitted December 17, 2002.) The relationship between the LSPR extinction maximum (λ_{max}) and the SERS enhancement factor (EF) was explored in detail using the innovative approach of plasmon sampled surface-enhanced Raman excitation spectroscopy (PS-SERES). PS-SERES studies were performed as a function of excitation wavelength, molecular adsorbate, vibrational band, and molecule-localized resonance or non-resonance excitation. In each case, high S/N ratio spectra are achieved for samples with an LSPR λ_{max} within a ~120 nm window that encompasses both the excitation wavelength and the scattered wavelength. These results unambiguously demonstrate a systematic approach to the optimization of SER spectra on nanoparticle substrates with large interparticle

spacings and consequently, weak or no electromagnetic coupling. In fact, this work demonstrates the largest SERS, $EF > 1 \times 10^8$, and SERRS, $EF > 7 \times 10^9$, enhancement factors measured to date on nanostructured substrates.

A breakthrough in glucose biosensor research enabled by surface-enhanced Raman spectroscopy (SERS) has been achieved (C. L. Haynes, M. R. Glucksberg, R. P. Van Duyne, *J. Am. Chem. Soc.*, **125**, 588-593 (2003)). The SERS glucose biosensor has a number of unique and important characteristics in its operational feature set. These include: (1) excellent sensitivity in the clinically important 1-25 mM range; (2) the ability to be miniaturized to the 1-10 μm x 1-10 μm level so that the sensor head is minimally invasive; (3) a direct and reversible sensing mechanism so that no chemical or enzymatic reagents are required or consumed; and (4) the potential to exhibit fast time response on the ~ 10 millisecond time scale so that a continuous readout is possible that could control an implanted insulin pump. So far as we are aware, no other glucose sensing technology possesses these desirable attributes. This SERS-based nanobiosensor approach provides a pathway to ultrasensitive biodetection experiments with low-cost instrumentation that will greatly facilitate field portable detection of a broad spectrum of Chem/Bio agents, environmental studies, and soldier medical diagnostic applications.

4. HyperRayleigh Spectroscopy.

We experimentally demonstrated for the first time the existence of distinguishable contributions to hyper-Rayleigh scattering (HRS) intensities from Ag nanoparticles arising from electric-dipole and electric-quadrupole plasmon resonances at the emitted wavelength. We showed that these results can be successfully modeled using an electromagnetic theory of HRS which assumes a surface-induced nonlinear susceptibility. In addition, we found that angular distribution measurements can be used to determine the relative sizes of the dipole and quadrupole contributions.

Our studies of hyper-Rayleigh intensities for copper, silver, gold and platinum demonstrated that for 800 nm excitation, silver gives the highest HRS intensity, with gold and copper being comparable, and much greater than platinum. Scattering efficiency factors, expressed as $\langle\beta^2\rangle/\text{atom}$ are significantly higher for silver than for the best molecular second harmonic chromophores.

5. Methods for Synthesizing Nanoparticles.

We developed new condensed phase synthetic strategies for fabricating, for the first time, disk shaped Ag nanoparticles, donut-shaped Ag nanoparticles, and other electromagnetically and topologically interesting nanoparticles. The particles shape has a profound effect upon their linear optical properties. Ag disks, for example, are intensely purple, while spheres are yellow. Discrete-dipole-approximation calculations replicate the experimental observations and provide detailed polarization and mechanistic information about plasmon resonances responsible for the chromophoric properties.

6. Preparation of Optical Multilayer Films

The research carried out in this area fell into the following areas:

- a Computer modeling of the properties of one-dimensional photonic materials;
- b Studies of enhanced luminescence in ZnO thin films and nanophase powders;
- c Development of reactive-ion-etching techniques to pattern substrates under nanosphere lithography masks

These topics will be discussed in this order below.

a. Computer modeling of the properties of one and two-dimensional photonic materials.

One goal of our program was to make one dimensional Bragg resonators, which can also be thought of as one-dimensional photonic crystals. One can reduce the interaction length for second harmonic generation if the electric field of the light is enhanced by making the structure resonant. If it is simultaneously resonant at both the fundamental and second harmonic the effect is further enhanced. We have developed a technique for making doubly resonant structures; it involves creating a special sequence from two materials but with four different sub-layer thicknesses in a period. By controlling these parameters one can independently adjust the band gap at the first and second Brillouin zone edges so that the fundamental and second harmonic are simultaneously resonant, even in the presence of material dispersion. A detailed numerical simulation of the behavior of such a device was carried out. It was found that the second harmonic generation efficiency increases as the eighth power of the number of layers.

b. Studies of enhanced luminescence in ZnO thin films and nanophase powders

Workers at Northwestern (Cao, Chang and Ho) have recently reported random lasing in powdered samples and in laser-ablated thin films of ZnO. Since we were already committed to making ZnO films in connection with the above described program, we reproduced some of the observed behaviors in both films, prepared by the oxidization of e-beam and sputtered metallic Zn, and in pressed powders of nanophase ZnO, including studies of the temperature dependence. The whole topic of random lasing is still controversial and we take no position now as to whether the observed effects do or do not correspond to this phenomena. A possible alternative interpretation is that it arises from bound exciton states in the nanocrystalline materials involved. There is currently much interest in exciton phenomena in confined geometries and there appears to be some potential for making optical devices. Most of the work involves weakly bound excitons in materials like GaAs; thermal ionization then confines the observations to low temperatures, which limits the device potential. In collaboration with D. Snoke of the University of Pittsburgh we started a collaboration involving strongly bound excitons in materials like ZnO.

c. Development of reactive-ion-etching techniques to pattern substrates under nanosphere lithography masks

In a collaboration involving the Ketterson and Van Duyne groups, graduate students Christy Haynes and Grant Kiehne developed a number of procedures that promise to increase the effectiveness and the range of applicability of nanosphere lithography. Here we describe only two of these new directions, both involving the combination of nanosphere lithography and reactive ion etching. Depending on the etchant, one can either etch the underlying substrate (in the spaces outside the “shadow” cast by the polystyrene spheres) or (using an oxygen plasma) reduce the size of the spheres themselves; both were achieved. As a part of this MURI’s activities, Professor VanDuyne has demonstrated a number of very favorable properties, useful for a number of applications, which exploit the enhanced electrical fields associated with the plasmons excited on the

pyramids resulting from deposition through a nanosphere mask. For some applications (e.g. enhanced second harmonic generation where the intense fields tend to blow the Ag particles off of the surface) it would be desirable to recess the Ag structures below the level of the substrate. With the freedom to *re-etch* the substrate (precisely where the Ag will be deposited) it is now possible to “bury” the particles.

The ability to etch down the size of the polyballs (in-place, without disturbing their locations and by a controlled amount) allows one to deposit some material that will now surround each ball, forming an interconnected honeycomb. In practice this would be a material that can be lifted off by a subsequent process. The balls can then be “dissolved off” and a second material deposited, followed by lifting off the honey-comb. This results in a near-perfect array of discs of the second material.

7. Theory: Molecular Optical Properties. One of the major DoD interests involving molecular structures has been optical properties, particularly laser hardening, nonlinear optical response, light emission for displays and detection/logic circuits. In the purely molecular area, we have completed significant studies on the control of optical properties by molecular structure. These have included the first analysis of triplet/triplet absorption spectra, both for comparison with stable darkening agents and for understanding the residual absorption mechanism for optical emitting. We found both some formal results (several levels of configuration interaction are necessary for such response properties to converge, and there is great sensitivity in molecular electronic structure to the geometric structure of the excited states) and some physically important examples of extended pi-type chromophores that exhibit strong triplet absorptions.

Other papers in the general area of molecular optical properties included prediction of extremely strong two-photon absorption when double resonances occur (that means that two excited states are spaced equally). Finally, in work which is about to be published, Geoff Hutchison (a graduate student) has completed a set of calculations on extended oligomers and periodic systems, demonstrating that the general scaling laws used to predict polymer properties from oligomer properties need to be corrected by an extra term scaling with the box length, that corresponds to end effects. With this, it is possible to get an extremely accurate prediction of polymer properties on the basis of scaling from small oligomer calculations.

8. Combined Optics and electronics - light emitting diode structures. LEDs based on organics are important for displays, for large format lighting applications, and (at the nano level) as a possible memory element. They also pose a complex theoretical problem because it is necessary to produce the excited state, and also to optimize the emission in the desired wave length and polarization range. We produced a number of significant attacks on the LED problem, including prediction of situations under which the statistical limitation of 0.25 as the maximum photon yield can be exceeded, analyses of quenching at the metal interface and how to prevent it by the use of thin films of semiconductors or insulators, and a collaborative project on the optimization of emission yield utilizing balance of electron and hole currents. We also published general formal analyses of scaling in random media, and an analysis of the competition between space charge limited and injection limited currents.

9. Theoretical Studies of Nanoparticle Optical Properties

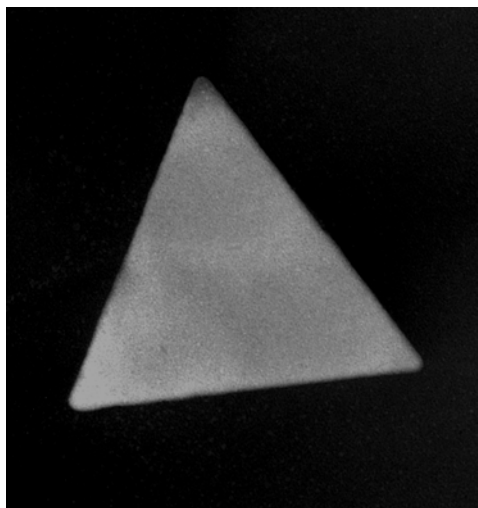


Figure 6. Silver nanoparticle with the shape of a triangular prism.

A. Discrete Dipole Approximation Studies of Individual Nanoparticles

An important accomplishment of the MURI program was the development of computational methods for describing the optical properties of metal nanoparticles, of nanoparticles in complex environments, and of arrays and aggregates of nanoparticles. For isolated particles the workhorse of the methods we developed was the Discrete Dipole Approximation (DDA). This divides the particle into polarizable finite elements (i.e., cubes) that couple to the incident field and to each other through their induced dipole moments. The collective response of the entire object is then determined, and from this the extinction cross section are calculated. This approach generally provides about 90% of the correct spectral response, independent of particle size or shape, once the results are converged with respect to the number of dipoles. The error here arises from assumptions

made in representing the induced polarization using finite elements, but the error is small enough that more accurate results have not been needed.

As a superb example of what can be done using the DDA approach for isolated particles, we have studied triangular prism-shaped silver particles that were fabricated by the Mirkin group using a special wet-chemistry method. TEM pictures of particles, Figure 6, show that most of the particles are triangular prisms with an edge dimension of about 100 nm and a thickness of about 15 nm. Many of the triangles have tips that are truncated, but the picture shows remarkable uniformity for particles that are made by strictly chemical methods. Figure 7 shows that the extinction spectra of these particles have three distinct peaks, at 640 nm, 470 nm and 335 nm, which is the first time that three distinct plasmon resonances have been seen for isolated nanoparticles.

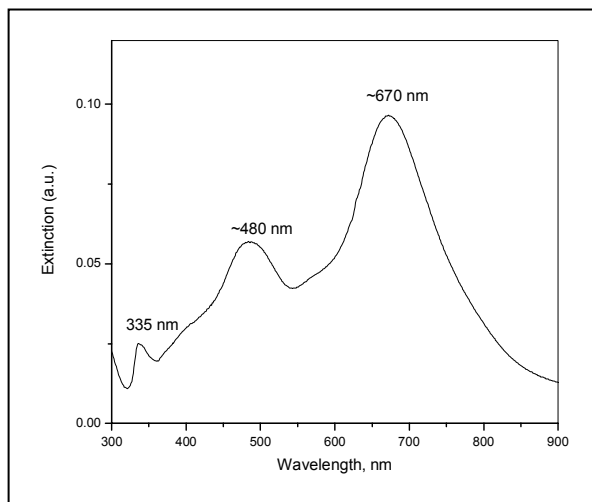
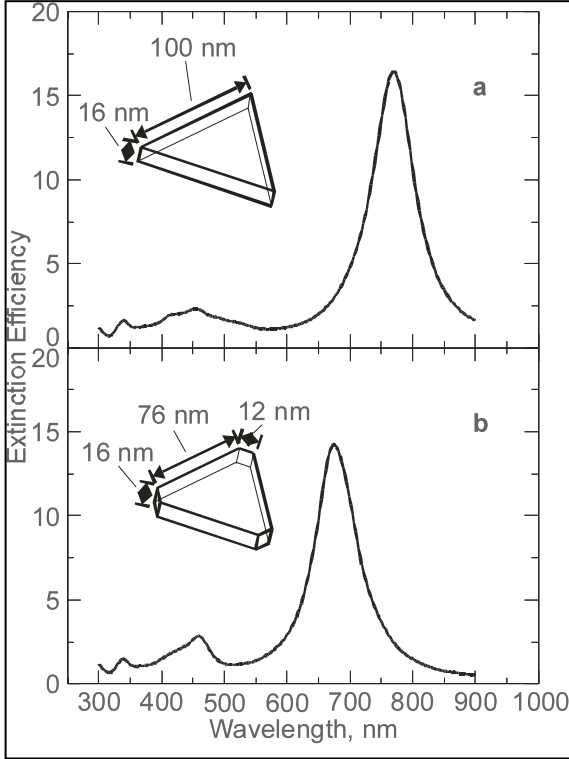


Figure 7. Observed extinction of triangular prisms.

Figure 8. Calculated spectrum of triangular prism for



Our DDA results for the triangular prisms are presented in Figure 8. In this figure, the top panel shows the spectrum obtained for a perfect triangular prism, while the bottom shows results for a prism in which the tips have been truncated. This figure shows better agreement with experiment for the truncated tip, but even the perfect triangular prism shows the same three spectral features as seen in the experiment. An analysis of the induced polarizations indicates that the 640 nm resonance arises from the usual dipole plasmon resonance that is seen for spheres, with this resonance being associated with polarization that is in the plane of the prism. The resonance at 470 is associated with in-plane quadrupole excitation of the polarization, while that at 335 nm is an out-of-plane quadrupole excitation. There is an out-of-plane resonance at 440 nm that shows up as a minor bump in the theory results, but it is too weak to be seen in the measurements. Overall these results provide a dramatic demonstration of quadrupole resonance effects, including the first observation of multiple quadrupole resonances for any particle. This unexpected result has potentially important implications for extinction and Raman-based sensing applications that we are currently studying.

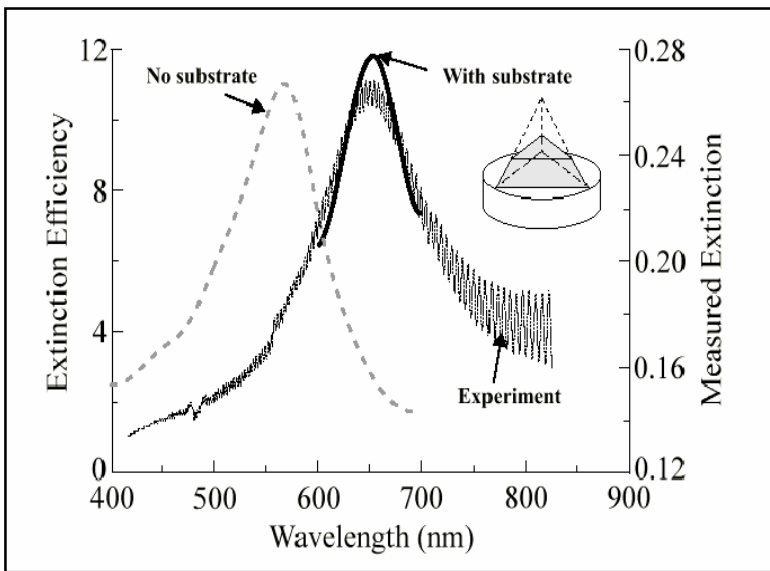


Figure 9. Measured and calculated extinction spectra of a truncated tetrahedron silver particle.

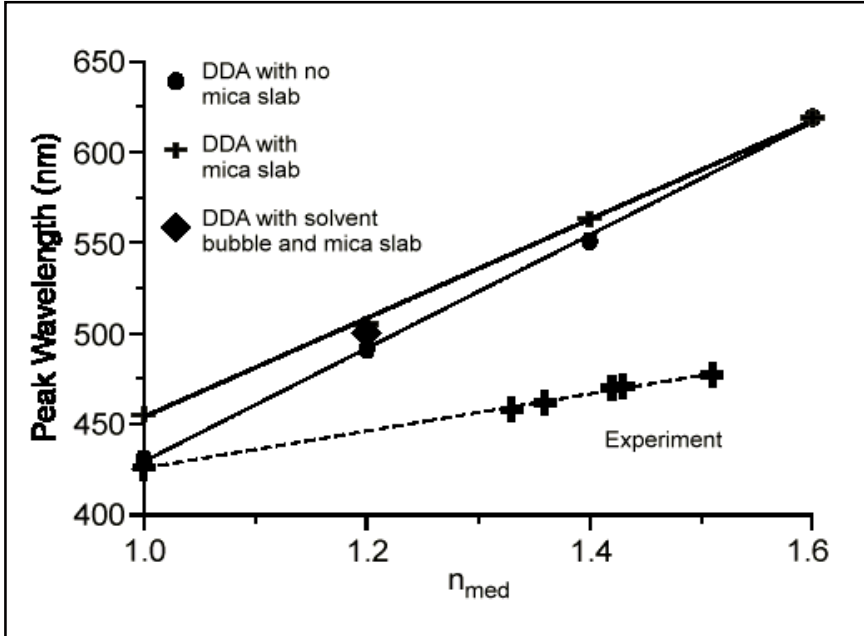


Figure 10. Plasmon peak wavelength version solvent index of refraction, including experimental results for silver particles, and theoretical (DDA) results with various models for the substrate slab and for surrounding solvent.

B. Theoretical studies of nanoparticle substrate and solvent effects

Another important result of our electrodynamics studies was our use of the DDA method to describe the influence of substrate and solvent on the nanoparticle extinction spectra. Figure 9 shows a very stunning example of the effect of substrate on the localized surface plasmon resonance. In this example, we compare the results of measurements on a triangular particle (here modeled as a truncated

tetrahedron) with a footprint of 100 nm, and a height of 35 nm, with the results of DDA calculations for the particle with and without a mica substrate. To include the mica substrate in the calculation, we have generalized the DDA method to include both silver and mica finite elements, with the mica being represented as a cylinder with dimensions that are approximately twice the footprint of the particle, and the same height. Previously we have shown that a chunk of substrate of roughly these dimensions is sufficient to give converged optical properties. What the figure shows is that there is a very significant red shift in the spectra resulting from the substrate effect, and that the DDA spectrum that includes it is in essentially perfect agreement with experiment. We also find that the substrate effect is the most significant for particles with the largest aspect ratio, and of course the substrate effect gets larger for substrates with larger dielectric constants. These results are consistent with those from experiments that are described above.

The DDA approach to substrates also gives us several methods for including solvent effects in the theoretical modeling of PPA extinction spectra. In Figure 10 we present results from calculations of this sort along with selected experimental results that were taken Van Duyne's work. The simplest DDA method includes for the solvent as bulk continuum, but without including substrate effects. Unfortunately this approach seriously overestimates the substrate shift compared to experiment. A second approach is to include both the particle and a cylinder of substrate, and

then the solvent is added as a bulk continuum. A third approach involves including a finite droplet of solvent, with its dielectric constant, along with the particle and substrate explicitly in the DDA calculation. Fig. 10 shows that the second and third approaches give similar results, and both represent an improvement over the first in comparison with experiment. Unfortunately, none of the results match experiment quantitatively. One likely reason for this is that it arises from an oxide coating of the particle surface that occurs spontaneously when the particle is synthesized. (This is a well known impediment in ellipsometry measurements.) Surrounding the particle with a self-assembled monolayer leads to a dramatic change in this behavior such that the experimental slope is now higher than the theory. Charge transfer interactions between the particle and its surroundings are a likely reason for this, showing that getting theory and experiment to agree on this property is difficult.

D. Magnetic Nanoparticles (de Heer, Ketterson, Van Duyne)

1. Introduction

This group was concerned with the development of new kinds of magnetic materials for use in permanent magnets and as high density nonvolatile memory in computers. There were two components to this project. In the first we used molecular beam methods to prepare and characterize the properties of single magnetic nanoparticles. The second part was concerned with making arrays of magnetic nanoparticles using electron-beam lithography, and characterizing the magnetic properties of these arrays with magnetic force microscopy, and ferromagnetic resonance spectroscopy.

2. Molecular beam experiments on magnetic clusters.

We built a molecular beam machine for studying the magnetic properties of metal and metal oxide nanoparticles (see Fig. 11). The cryogenic source is a laser vaporization cluster source which operates at temperatures as low as 5 K, using the closed cycle He refrigerator. A breakthrough was achieved in the development of a pulsed valve which operates entirely at the low temperature, to ensure that the clusters are equilibrated at that temperature. This advancement not only impacts magnetism but will have important consequences for the entire field. It should be noted that free nanoscopic particles with fewer than about 100 atoms will be in their electronic and vibrational ground states when their temperature is below about 15 K. This means that there is no advantage to reducing the temperatures even lower than that as far as the interrogation of temperature dependent properties is concerned. The new source is also particularly bright. Further improvements include extensions of the Excimer laser for VUV (159 nm) operation, which significantly enhances the ionization capability and the development of a chopper for precision velocity measurements (which is required for precise magnetic moment measurements).



Figure 11. Molecular beam apparatus for measuring the magnetic properties of atomic clusters.

Niobium diamagnetism. We have performed magnetic measurements on Niobium clusters that has revealed that odd numbered clusters are paramagnetic (Fig. 12). For the small odd clusters, the Stern Gerlach experiments exhibit symmetric deflections which reflect the unpaired electron spin in these systems. This is significant, since the spin relaxation, which is observed in ferromagnetic clusters is not observed in this system. The reason is to be found in the coupling of the spin to the cluster framework, which is very strong in ferromagnetic systems and (most likely) very weak in Nb clusters.

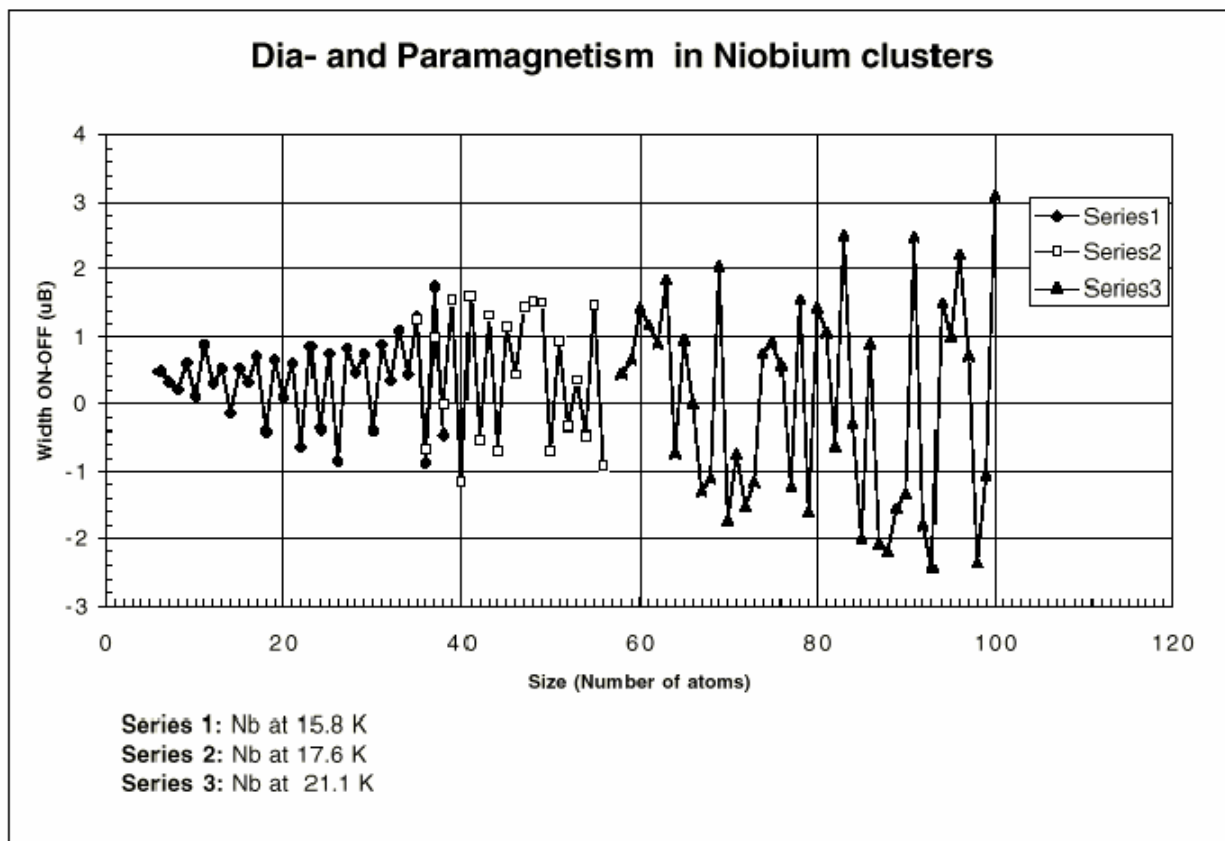


Figure 12. Magnetic moment as function of cluster size for Ni clusters.

Cobalt Ferromagnetism . We have measured the magnetic moments of Co clusters (from the atom to 100 atom clusters) as a function of temperature (Fig. 13). We have found that at low temperatures the magnetic moment reduces (in contrast to bulk ferromagnetism). This effect is most likely caused by the coupling of the spin to the cluster, which corresponds to the blocking of the spin in superparamagnetic systems. In this system however, it causes a reduction in the magnetization.

We also found that the smallest cluster which shows single-sided ferromagnetic deflections is Co_5 : all clusters larger than this deflect in the direction of increasing magnetic field even at cryogenic temperatures. This is important since it is clear that spin relaxation is not involved since phonons are required for spin relaxation. Nevertheless, there the deflections do depend on the source temperature. This signals that, what previously was interpreted to be intermolecular spin relaxation is in fact a static property of the ferromagnetic clusters: there is no relaxation time. This phenomenon may relate to macroscopic spin tunneling effects which have recently been observed in spin carrying molecules.

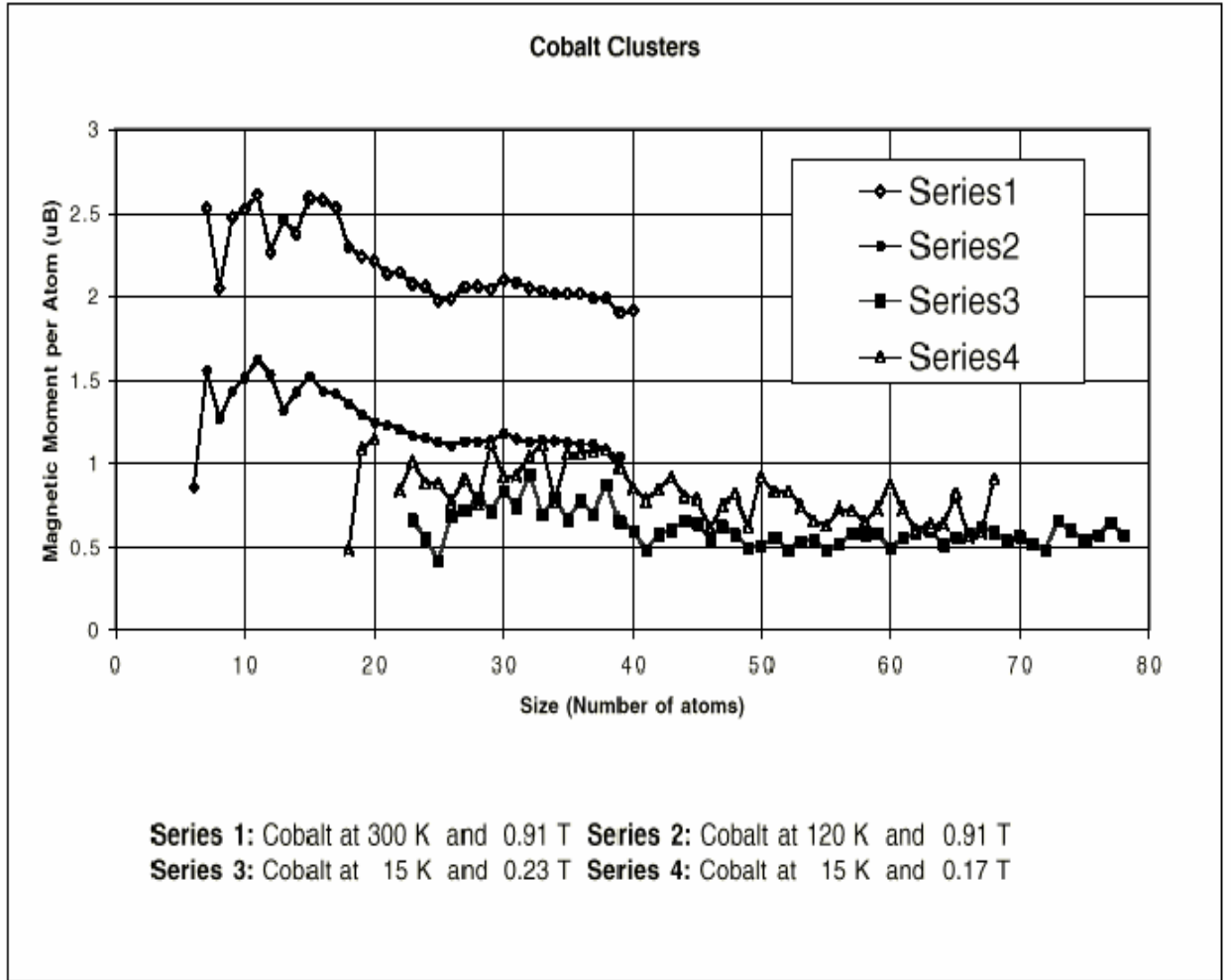


Figure 13. Magnetic moment of Co clusters as function of size.

3. Magnetic nanoparticle arrays

We patterned arrays of Nb, Fe, Ni and Co dots approximately 1000Å in diameter and with a 2d lattice spacing of 1 micron using e-beam lithography. Ferromagnetic resonance and magnetic force microscopy was used to characterize the magnetic properties of these arrays. The field dependent transport properties of superconducting niobium films, which are modulated by a regular array of non-magnetic and magnetic normal-metal inclusions (dots), was published. Strong peaks in the critical current were seen for fields at which the vortex density in the superconductor is some rational or sub-rational multiple of the dot density. This commensurate peak effect is enhanced for the magnetic dot arrays when the dots are magnetized in a direction parallel to the applied magnetic field and suppressed when they are anti-aligned. Qualitative information on the strength of this dot-vortex interaction was inferred from the commensurate peaks present and missing for different regular lattices.

(6) Listing of all publications

A. Papers published in peer reviewed journals

Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Colorimetric DNA-Detection, Science*, **1997**, 277, 1078-1080.

A. A. Shvartsburg, L. A. Pederson, R. R. Hudgins, G. C. Schatz, and M. F. Jarrold, *Structures of the Clusters Produced by Laser Desorption of Fullerenes: [2+2] Cycloadducts of Pre-Shrunk Cages*, *J. Phys. Chem.*, **102**, 7919-23 (1998).

Stefan Frank, Philippe Poncharal, Z.L. Wang, Walt A de Heer, *Carbon Nanotube Quantum Conductors, Science*, **280**, 1744, (1998).

P. Freunscht, R. P. Van Duyne, S. Schneider, *Surface-Enhanced Raman Spectroscopy of trans-Stilbene Adsorbed on Silver Film over Nanosphere Surfaces Modified by Platinum or Alkanethiol Deposition*, *Chem. Phys. Lett.*, **281**, 372-378 (1997).

A. K. Ott, G. A. Rechtsteiner, C. Felix, O. Hampe, M. F. Jarrold, R. P. Van Duyne, K. Raghavachari, *Raman Spectra and Calculated Vibrational Frequencies of Size-Selected C₁₆, C₁₈, and C₂₀ Clusters*, *J. Chem. Phys.*, **109**, 9652-9655 (1998).

M.A. Ratner, B. Davis, M. Kemp, V. Mujica, A. Roitberg, S. Yaliraki, *Molecular Wires: Charge Transport, Mechanisms, and Control. Ann. N.Y. Acad. Sci.* **852**, 22-37 (1998).

A. A. Shvartsburg, M. F. Jarrold, B. Liu, Z.-Y. Lu, C.-Z. Wang, and K.-M. Ho, *Dissociation Energies of Silicon Clusters: A Depth Gauge for the Global Minimum on the Potential Energy Surface*, *Phys. Rev. Lett.*, **81**, 4616-4619(1998).

B. Liu, A. A. Shvartsburg, Z.-Y. Lu, B. Pan, C.-Z. Wang, K.-M. Ho, and M. F. Jarrold, *Ionization of Medium-Sized Silicon Clusters and the Geometries of the Cations*, *J. Chem. Phys.*, **109**, 9401-9409 (1998).

S.N. Yaliraki, M.A. Ratner, *Molecular-interface coupling effects on electronic transport in molecular wires. J. Chem. Phys.* **109**, 5036-5043 (1998).

Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *One-Pot Colorimetric Differentiation of Polynucleotides with Single Base Imperfections Using Gold Nanoparticle Probes*, *J. Am. Chem. Soc.*, **120**, 1959-1964 (1998).

Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L. *DNA-Directed Synthesis of Binary Nanoparticle Network Materials*, *J. Am. Chem. Soc.*, **120**, 12674-12675 (1998).

F. W. Vance, B. I. Lemon, and J. T. Hupp, *Enormous Hyper-Rayleigh Scattering from Nanocrystalline Gold Particle Suspensions*, *J. Phys. Chem. B*, **102**, 10091-10093 (1998).

A. K. Williams and J. T. Hupp, *Sol-Gel Encapsulated Alcohol Dehydrogenase as a Versatile, Environmentally Stabilized Sensor for Alcohols and Aldehydes*, *J. Am. Chem. Soc.*, **120**, 4366-4371 (1998).

F. W. Vance, B. I. Lemon, J. A. Ekhoﬀ, and J. T. Hupp, *Interrogation of Nanoscale Silicon Dioxide/Water Interfaces via Hyper-Rayleigh Scattering*, *J. Phys. Chem. B*, **102**, 1845-1848 (1998).

Gary S. Kedziora and George C. Schatz, *Calculating Dipole and Quadrupole Polarizabilities Relevant to Surface Enhanced Raman Spectroscopy*, *Spectrochimica Acta*, **A55**, 625-638, (1999).

T. R. Jensen, G. C. Schatz and R. P. Van Duyne, *Nanosphere lithography: Surface plasmon resonance spectrum of a periodic array of silver nanoparticles by UV-vis extinction spectroscopy and electrodynamic modelling*, *J. Phys. Chem.*, **B103**, 2394-2401(1999)

T. R. Jensen, M. L. Duval, K. L. Kelly, A. Lazarides, G. C. Schatz and R. P. Van Duyne, *Electrodynamics of Noble Metal Nanoparticles and Nanoparticle Clusters, Nanosphere lithography: effect of the external dielectric medium on the surface plasmon resonance spectrum of a periodic array of silver nanoparticles*, *J. Phys. Chem.*, **103**, 9846-53 (1999).

T. Jensen, L. Kelly, A. Lazarides and G. C. Schatz, *Electrodynamics of Noble Metal Nanoparticles and Nanoparticle Clusters*, *J. Cluster Science*, **10**, 295-317 (1999).

J. C. Hulteen, D. A. Treichel, M. T. Smith, M. L. Duval, T. R. Jensen, R. P. Van Duyne, *Nanosphere Lithography: Size-Tunable Silver Nanoparticle and Surface Cluster Arrays*, *J. Phys. Chem.* **B103**, 3854-3863 (1999).

G. T. Kiehne, A. E. Kryukov, and J. B. Ketterson, *A Numerical Study of Optical Second Harmonic Generation in a One Dimensional Photonic Structure*, *Appl. Phys. Letters*, **75**, 1676 (1999).

A. A. Shvartsburg, B. Liu, Z.-Y. Lu, M. F. Jarrold, and K.-M. Ho, *Structures of Germanium Clusters: Where the Geometries of Silicon and Germanium Clusters Diverge*, *Phys. Rev. Lett.*, **83**, 2167-2170 (1999)

A. A. Shvartsburg, R. R. Hudgins, R. Gutierrez, G. Jungnickel, T. Frauenheim, K. A. Jackson, and M. F. Jarrold, *Ball and Chain Dimers from a Hot Fullerene Plasma*, *J. Phys. Chem.*, **A103**, 5275-5284 (1999).

A. A. Shvartsburg and M. F. Jarrold, *Tin Clusters Adopt Prolate Geometries*, *Phys. Rev.* **A60**, 1235-1239 (1999).

R. C. Mucic, J. J Storhoff, C. A Mirkin, and R. L. Letsinger, *DNA-Directed Synthesis of Binary Nanoparticle Network Materials*, *J. Am. Chem. Soc.* **120**, 12674-12675 (1998).

R. L. Letsinger, C. A. Mirkin, R. Elghanian, R. C. Mucic, and J. J Storhoff, *Chemistry of Oligonucleotide-Gold Nanoparticle Conjugates, Phosphorus, Sulfur, and Silicon* **359-362** 144-146 (1999).

J. J. Storhoff and C. A. Mirkin, *Programmed Materials Synthesis with DNA*, *Chem. Rev.* **99**, 1849-1862 (1999).

K. J Watson, J. Zhu, S. Nguyen, and C. A. Mirkin, *Hybrid Nanoparticles With Block Copolymer Shell Structures*, *J. Am. Chem. Soc.* **121**, 462-463 (1999).

G. P. Mitchell, C. A. Mirkin, and R. L. Letsinger, *The Programmed Assembly of DNA Functionalized Quantum Dots*, *J. Am. Chem. Soc.* **121**, 8122-8123 (1999).

P. Poncharal, Z.L. Wang, D. Ugarte and W.A. de Heer, *Electrostatic deflections and electromechanical resonances of carbon nanotubes*, *Science*, **283**,1513 (1999).

W.A. de Heer, *Recent Developments in Carbon Nanotubes*, *Current Opinion in Solid State & Materials Science* **4**, 355-9 (1999).

S. N. Yaliraki, M. Kemp and M. A. Ratner, *Conductance of Molecular Wires: Influence of Molecule-Electrode Binding*, *J. Am. Chem. Soc.* **121**, 3428-34 (1999).

G. Ashkanazi, R. Kosloff and M. A. Ratner, *Photoexcited Electron Transfer: Short-Time Dynamics and Turnover Control by Dephasing, Relaxation, and Mixing*, *J. Am. Chem. Soc.* **121**, 3386-95 (1999).

S. N. Yaliraki, A. E. Roitberg, C. Gonzalez, V. Mujica and M. A. Ratner, *The injecting energy at molecule/metal interfaces: Implications for conductance of molecular junctions from an ab initio molecular description*, *J. Chem. Phys.* **111**, 6997-7002 (1999).

Mirkin, C. A. *Towards DNA Based Technology for Preparing Nanocluster Circuits and Arrays*, *MRS Bulletin*, **25**, 43-54 (2000).

Mirkin, C. A. *Programming the Assembly of Two- and Three-Dimensional Architectures with DNA and Nanoscale Inorganic Building*, *Inorganic Chemistry* **39**, 2258-2272 (2000).

Letsinger, R. L.; Elghanian, R.; Viswanadham, G.; Mirkin, C. A. *Use of Steroid Cyclic Disulfide Anchor in Constructing Gold Nanoparticle-Oligonucleotide Conjugates*, *Bioconjugate Chemistry* **11**, 289-291 (2000).

Storhoff, J. J.; Lazarides, A. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L., Schatz, G.C. *What Controls the Optical Properties of DNA-linked Gold Nanoparticle Assemblies?* *J. Am Chem. Soc.* **122**, 4640-4650 (2000).

Reynolds, R. A. III; Mirkin, C. A.; Letsinger, R. L. *Homogeneous, Nanoparticle-Based Quantitative Colorimetric Detection of Oligonucleotides*, *J. Am. Chem. Soc.* **122**, 3795-3796(2000).

Reynolds, R. A.; Mirkin, C. A.; Letsinger, R. L. *A Gold Nanoparticle/latex Microsphere based Colorimetric Oligonucleotide Detection Method*, *Pure Appl. Chem.* **72**, 229-235 (2000).

Taton, T. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *The DNA-Mediated Formation of Supramolecular Mono- and Multilayered Nanoparticle Structures*, *J. Am. Chem. Soc.* **112**, 6305-6306 (2000).

Taton, T. A.; Mirkin, C. A.; Letsinger, R. L. *Scanometric DNA Array Detection with Nanoparticle Probes*, *Science* **289**, 1757-1760 (2000).

Demers, L. M.; Mirkin, C. A.; Mucic, R. C.; Reynolds, R. A.; Letsinger, R. L., Elghanian, R., Viswanadham G. *Fluorescence-Based Method for Determining the Surface Coverage and Hybridization Efficiency of Thiol-Capped Oligonucleotides Bond to Gold Thin Films and Nanoparticles*, *Analytical Chemistry* **72**, 5535-5541 (2000).

Park, S. J.; Lazarides, A. A.; Mirkin, C. A.; Brazis, P.W.; Kannewurf, C. R.; Letsinger, R. L.; *The Electrical Properties of Gold Nanoparticle Assemblies Linked by DNA*, *Angewandte Chemie* **39**,3845-3848 (2000).

Mirkin, C. A. *Bioinspired Two- and Three-Dimensional Nanostructures*, *Journal of Nanoparticle Research* **2**,121-122 (2000).

Mirkin, C. A.; Taton, T.A. *Semiconductors Meet Biology*, *Nature* **405**, 626-627 (2000).

Taton, T. A.; Mirkin, C. A. *Haplotyping by Force*, *Nature Biotechnology* **18**, 713 (2000).

A. A. Lazarides and G. C. Schatz, *DNA-linked metal nanosphere materials: structural basis for the optical properties*, *J. Phys. Chem.* **104**, 460-7 (2000).

A. A. Lazarides and G. C. Schatz, *DNA-linked metal nanosphere materials: FFT solution for the optical response*, *J. Chem. Phys.* **112**, 2987-2993(2000).

Anne A. Lazarides, K. Lance Kelly, Traci R. Jensen and George C. Schatz, *Optical Properties of Metal Nanoparticles and Nanoparticle Aggregates Important in Biosensors*, *Theochem*, **529**, 59-63 (2000).

Karen Drukker and G. C. Schatz, *A model for simulating dynamics of DNA Denaturation*, *J. Phys. Chem.* **104**, 6108-11 (2000).

DL Albert, T.J. Marks, M.A. Ratner, R.D. Rauh, *Optical limiting chromophores. Correlation effects in computing triplet-triplet absorption energies of organic molecules*. *J. Phys. Chem. A* **104**, 837-844 (2000).

A.L. Burin, M.A. Ratner, *Exciton Migration and Cathode Quenching in Organic Light Emitting Diodes*. *J. Phys. Chem. A* **104**, 4704-4710 (2000).

V. Mujica, A.E. Roitberg, M. Ratner, *Molecular Wire Conductance: Electrostatic Potential Spatial Profile*. *J. Chem. Phys.* **112**, 6834-6839 (2000).

A.L. Burin, M.A. Ratner, *Temperature and field dependence of the charge injection from metal electrodes into random organic media*. *J. Chem. Phys.* **113**, 3941-3944 (2000).

Y.A. Berlin, A.L. Burin, M.A. Ratner, *DNA as a molecular wire. Superlattices and Microstructures* **28**, 241-252 (2000).

Z.L. Wang, P. Poncharal, and W.A. de Heer, *Nanomeasurements in Transmission Electron Microscopy*, *Microscopy and Microanalysis* **6**, no.3 p.224-30, 2000.

Z.L. Wang, P. Poncharal, and W.A. de Heer, *Measuring Physical and Mechanical Properties of Individual Carbon Nanotubes by In-Situ TEM*, *Journal of the Physics and Chemistry of Solids* **61**, no.7 p.1025-30, 2000.

Gao, R.; Wang, Z.L.; Zhigang Bai; de Heer, W.A.; Liming Dai; Mei Gao, *Nanomechanics of individual carbon nanotubes from pyrolytically grown arrays*, *Physical Review Letters* **85**, no.3 p.622-5, 2000.

R.P. Gao, Z.L. Wang, Z.G. Bai, W. de Heer, L. Dai and M. Gao, *Nanomechanics of Aligned Carbon Nanotube Arrays*, *Physical Review Letters* **85**, no.3 p.622-5, 2000.

T. R. Jensen, R. P. Van Duyne, S. A. Johnson, V. A. Maroni, *Surface-Enhanced Infrared Spectroscopy: A Comparison of Metal Island Films with Discrete and Non-Discrete Surface Plasmons*, *Appl. Spectrosc.*, **54**, 371-377 (2000).

T. R. Jensen, M. Duval Malinsky, C. L. Haynes, R. P. Van Duyne, *Nanosphere Lithography: Tunable Localized Surface Plasmon Resonance Spectra of Silver Nanoparticles*, *J. Phys. Chem. B*, **104**, 10549-10556 (2000).

L. A. Dick, A. J. Haes, R. P. Van Duyne, *Distance and Orientation Dependence of Heterogeneous Electron Transfer: A Surface-Enhanced Resonance Raman Scattering Study of*

Cytochrome c Bound to Carboxylic Acid Terminated Alkanethiols Adsorbed on Silver Electrodes, *J. Phys. Chem. B*, **104**, 11752 - 11762 (2000).

J. P. Novak, L. C. Brousseau, F. W. Vance, R. C. Johnson, B. I. Lemon, J. T. Hupp, D. L. Feldheim, *Nonlinear Optical Properties of Molecularly Bridged Gold Nanoparticle Arrays*. *J. Am. Chem. Soc.* **122**, 12029-12030, **2000**,

A. Terentiev, D. B. Watkins, L. E. De Long, D. E. Morgan, and J. B. Ketterson, *Periodic magnetization instabilities in a superconducting Nb film with a square lattice of Ni dots*, *Phys. Rev.* **B61**, R9249 (2000).

A. Terentiev, B. Watkins, L. E. De Long, et al., *Periodic magnetization instabilities in a superconducting Nb film with a square lattice of Ni dots*, *Physica C* **332**, 5 (2000).

G. T. Kiehne, M. Z. Lin, G. Wang, W. H. Xiang, H. Cao, and J. B. Ketterson, *A Pulser for Medium-Frequency Direct-Current Reactive Sputter-Deposition of Insulators*, *Rev. Sci. Instr.* **71**, 2560-2 (2000).

Y. Sun, J. B. Ketterson and G. K. Wong, *Excitonic gain and stimulated ultraviolet emission in nanocrystalline ZnO*, *Appl. Phys. Lett.* **77**, 2322 (2000).

A. A. Shvartsburg and M. F. Jarrold, *The Covalent to Metallic Transition in Group 4 Clusters*, *Chem. Phys. Lett.*, **317**, 615-618, (2000).

A. A. Shvartsburg and M. F. Jarrold, *Solid Clusters Above the Bulk Melting Point*, *Phys. Rev. Lett.*, **85**, 2530-2533, (2000). Publicity: <http://sciencenow.sciencemag.org/cgi/content/full/2000/925/1>, <http://focus.aps.org/v6/st11.html>, and H. Haberland, *Tin Clusters Foil High Temperatures*, *Physics World*, **13**, 27-28, (2000).

A. A. Shvartsburg, B. Liu, M. F. Jarrold, and K.-M. Ho, *Modeling Ionic Mobilities by Scattering on Electronic Density Isosurfaces: Application to Silicon Cluster Anions*, *J. Chem. Phys.*, **112**, 4517-4526, (2000).

A. A. Shvartsburg, R. R. Hudgins, P. Dugourd, R. Gutierrez, T. Frauenheim, and M. F. Jarrold, *Observation of "Stick" and "Handle" Intermediates Along the Fullerene Road*, *Phys. Rev. Lett.* **84**, 2421-2424, (2000).

G. A. Rechtsteiner, C. Felix, A. K. Ott, O. Hampe, R. P. Van Duyne, M. F. Jarrold, K. Raghavachari, *Raman and Fluorescence Spectra of Size-Selected, Matrix-Isolated C₁₄ and C₁₈ Neutral Carbon Clusters*, *J. Phys. Chem. A*, **105**, 3029-3033 (2001).

M. Litorja, C. L. Haynes, A. J. Haes, T. R. Jensen, R. P. Van Duyne, *Surface-Enhanced Raman Scattering Detected Temperature Programmed Desorption: Optical Properties, Nanostructure*,

and Stability of Silver Films Over SiO₂ Nanospheres, *J. Phys. Chem. B*, 105, 6907-6915 (2001).

R. I. Altkorn, I. Koev, R. P. Van Duyne, M. Duval Malinsky, *Intensity Considerations in Liquid Core Optical Fiber Raman Spectroscopy*, *Appl. Spectrosc.*, 55, 373-381 (2001).

M. Duval Malinsky, L. Kelly, G. C. Schatz, R. P. Van Duyne, *Chain Length Dependence and Sensing Capabilities of the Localized Surface Plasmon Resonance of Silver Nanoparticles Chemically Modified with Alkanethiol Self-Assembled Monolayers*, *J. Am. Chem. Soc.*, 123, 1471-1482 (2001).

M. Duval Malinsky, L. Kelly, G. C. Schatz, R. P. Van Duyne, *Nanosphere Lithography: Effect of the Substrate on the Localized Surface Plasmon Resonance Spectrum of Silver Nanoparticles*, *J. Phys. Chem. B*, 105, 2343-2350 (2001).

C. L. Haynes, R. P. Van Duyne, *Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics*, *J. Phys. Chem. B*, 105, 5599-5611 (2001).

C. L. Haynes, A. D. McFarland, M. T. Smith, J. C. Hulteen, R. P. Van Duyne, *Angle-Resolved Nanosphere Lithography: Manipulation of Nanoparticle Size, Shape, and Interparticle Spacing*, *J. Phys. Chem. B*, 106, 1898-1902 (2002).

L. A. Dick, A. D. McFarland, C. L. Haynes, R. P. Van Duyne, *Metal Film Over Nanosphere (MFON) Electrodes for Surface-Enhanced Raman Spectroscopy (SERS): Improvements in Surface Nanostructure Stability and Suppression of Irreversible Loss*, *J. Phys. Chem. B*, 106, 853-860 (2002).

K. L. Kelly, A. A. Lazarides and G. C. Schatz, *Computational Electromagnetics of Metal Nanoparticles and Nanoparticle Aggregates*, *Computing in Science & Engineering* 3, 67-73 (2001) .

George C. Schatz, *Electrodynamics of Nonspherical Noble Metal Nanoparticles and Nanoparticle Aggregates*, *Theochem*, 573 73-80 (2001).

R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. -G. Zheng, *Photo-induced Conversion of Silver Nanospheres to Nanoprisms*, *Science*, 294, 1901-1903 (2001).

G. Wang, G. K. L. Wong, J. B. Ketterson, *Redetermination of second-order susceptibility of zinc oxide single crystals*, *Appl. Optics* **40**, 5436 (2001)

Park, S. J.; Lazarides, A. A.; Mirkin, C. A. *Directed Assembly of Periodic Materials from Protein and Oligonucleotide-Modified Nanoparticle Building Blocks*, *Angewandte Chemie*, 2001, 40, 2909-2912.

Cao, Y.; Jin R.; Mirkin, C. A. *DNA- Modified Core-Shell Ag/Au Nanoparticles*, *J. Am. Chem.*

Soc, 2001, 123, 7961-7962.

Park, S.J.; Taton, T.A.; Mirkin, C.A. *Array-Based Electrical Detection of DNA Using Nanoparticle Probes*, *Science*, 2002, ASAP Article, January 31, 2002.

Park, S. J.; Lazarides, A. A.; Mirkin, C. A.; Brazis, P.W.; Kannewurf, C. R.; Letsinger, R. L. *The Electrical Properties of Gold Nanoparticle Assemblies Linked by DNA*, *Angewandte Chemie* 2000, 39,3845-3848.

Watson, K.J.; Park, S.J.; Im, J.H.; Nguyen, S.T.; Mirkin, C.A. *DNA-Block Copolymer Conjugates*, *J. Am. Chem. Soc.*, 2001, 123, 5592-5593.

Taton, T.A.; Lu, G.; Mirkin C. A. *Two-color labeling of Oligonucleotide Arrays via Size-Selective Scattering of Nanoparticle Probes*, *J. Am. Chem. Soc* 2001, 123, 5164-5165.

G. A. Rechtsteiner, O. Hampe, and M. F. Jarrold, *Synthesis and Temperature Dependence of Hydrogen Terminated Silicon Clusters*, *J. Phys. Chem. B*, **2001**, 105, 4188-4194.

A. A. Shvartsburg, R. R. Hudgins, P. Dugourd, and M. F. Jarrold, *Structural Information from Ion Mobility Measurements: Applications to Semiconductor Clusters*, *Chem. Soc. Rev.*, **2001**, 30, 26-35.

S.K. Pati, T.J. Marks, M.A. Ratner, *J. Am. Chem. Soc.* **123**, 7287-7291 (2001). *Conformationally tuned Large Two-Photon Absorption Cross Sections in Simple Molecular Chromophores*.

A.L. Burin, Y.A. Berlin, M.A. Ratner, *J. Phys. Chem. A* **105**, 2652-2659 (2001). *Semiclassical Theory for Tunneling of Electrons Interacting with Media*.

Y. Xue, S. Datta, M.A. Ratner, *J. Chem. Phys.* **115**, 4292-4299 (2001). *Charge Transfer and "Band Lineup" in Molecular Electronic Devices: A Chemical and Numerical Interpretation*.

G.R. Hutchison, M.A. Ratner, T.J. Marks, *J. Phys. Chem. B* **105**, 2881-2884 (2001). *Adsorption of Polar Molecules on a Molecular Surface*.

Wang, Zhong L.; Gao, Rui Ping; de Heer, Walt A.; Poncharal, P. *In situ imaging of field emission from individual carbon nanotubes and their structural damage*. *Applied Physics Letters* (2002), **80**(5), 856-858.

Y. Kim, J. Li, R. C. Johnson, J. T. Hupp and G. C. Schatz, *Synthesis and linear extinction properties of gold-core/silver-shell nanoparticles: comparisons of theory and experiment*, *Chem. Phys. Lett.* **35**, 421-8 (2002).

Robert C. Johnson, Jiangtian Li, Joseph T. Hupp, and George C. Schatz, *Hyper-Rayleigh Scattering Studies of Silver, Copper, and Platinum Nanoparticle Suspensions*, Chem. Phys. Lett., **356**, 534-540 (2002).

Lance Kelly, Eduardo Coronado, Lin Lin Zhao, George C. Schatz, *The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape and Dielectric Environment*. J. Phys. Chem. B, ASAP (2003).

E. Hao, G. C. Schatz, R. C. Johnson and J. T. Hupp, *Hyper-Rayleigh scattering (HRS) from silver nanoparticles*, J. Chem. Phys. **117**, 5963-5 (2002).

B. J. Coe, J. A. Harris, I. Asselberghs, K. Clays, G. Olbrechts, A. Persoons, J. T. Hupp, R. C. Johnson, S. J. Coles, M. B. Hursthouse, and K. Nakatani, "Quadratic Nonlinear Optical Properties of N-Aryl Stilbazolium Dyes," *Adv. Funct. Mat.*, **2002**, 12, 110-116.

J.E. Malinsky, J.G.C. Veinot, G.E. Jabbour, S.E. Shaheen, J.D. Anderson, P. Lee, Andrew G. Richter, A.L. Burin, M.A. Ratner, T.J. Marks, N.R. Armstrong, B. Kippelen, P. Dutta, N. Peyghambarian, *Chem. Mater.* **14**, 3054-3065 (2002), "Nanometer-Scale Dielectric Self-assembly Processes for Anode Modification in Organic Light-Emitting Diodes. Consequences for Charge Injection and Enhanced Luminous Efficiency."

A.L. Burin, M.A. Ratner, H. Cao, S.H. Chang, *Phys. Rev. Letts.* **88**, 1-4 (2002). Random Laser in One Dimension".

A.L. Burin, Y.A. Berlin, A.Z. Patashinski, M.A. Ratner, J. Friedrich, *Physica B*, **316**, 321-323 (2002). "Fluctuations of Conformational States in Biological Molecules: Theory for Anomalous Spectral Diffusion Dynamics."

S.N. Yaliraki, M.A. Ratner, *Ann. N.Y. Acad. Sci.*, **960**, 153-162 (2002). "Interplay of Topology and Chemical Stability on the Electronic Transport of Molecular Junctions".

G.R. Hutchison, M.A. Ratner, T.J. Marks, *J. Phys. Chem. A* **106**, 10596-10605 (2002). "Accurate Prediction of Band Gaps in Neutral Heterocyclic Conjugated Polymers".

C. Gonzalez, V. Mujica, M.A. Ratner *Anns. NY Acad. Sci.* **960**, 163-176 (2002). "Modeling the Electrostatic Potential Spatial Profile of Molecular Junctions - The Influence of Defects and Weak Links".

L. A. Dick, A. D. McFarland, C. L. Haynes, R. P. Van Duyne, "Metal Film Over Nanosphere (MFON) Electrodes for Surface-Enhanced Raman Spectroscopy (SERS): Improvements in Surface Nanostructure Stability and Suppression of Irreversible Loss", *J. Phys. Chem. B*, **106**, 853-860 (2002).

A. J. Haes, R. P. Van Duyne, "A Nanoscale Optical Biosensor: Sensitivity and Selectivity of an

Approach Based on the Localized Surface Plasmon Resonance Spectroscopy of Triangular Silver Nanoparticles", *J. Am. Chem. Soc.*, **124**, 10596-10604 (2002).

C. L. Haynes, A. D. McFarland, M. T. Smith, J. C. Hulteen, R. P. Van Duyne, "Angle-Resolved Nanosphere Lithography: Manipulation of Nanoparticle Size, Shape, and Interparticle Spacing", *J. Phys. Chem. B*, **106**, 1898-1902 (2002).

K. Mitchell, C. L. Haynes, A. D. McFarland, R. P. Van Duyne, J. A. Ibers, "Tuning of Optical Band Gaps: Syntheses, Structures, Magnetic, and Optical Properties of CsLnZnSe₃ (Ln = Sm, Tb, Dy, Ho, Er, Tm, Yb, and Y)", *Inorg. Chem.*, **41**, 1199-1204. (2002).

J. C. Riboh, A. J. Haes, A. D. McFarland, C. Ranjit, R. P. Van Duyne, "A Nanoscale Optical Biosensor: Real Time Immunoassay and Nanoparticle Adhesion", *J. Phys. Chem. B*, **107**, ASAP Article, Web Release Date: January 29 (2003).

K. E. Shafer-Peltier, C. L. Haynes, M. R. Glucksberg, R. P. Van Duyne, "Toward a Glucose Biosensor Based on Surface-Enhanced Raman Scattering", *J. Am. Chem. Soc.*, **125**, 588-593 (2003).

B. Papers in non-peer-reviewed journals

Mirkin, C. A.; Ratner, M. A. *Superlattices*, McGraw-Hill Year Book of Science and Technology, **1998**, p. 388.

W.A. de Heer, *Nanomagnetism*, In *Characterization of Nanophase Materials*, Z.L. Wang ed., Wiley Wienhiem, 2000, 289-313.

R. C. Johnson and J. T. Hupp, *Hyper-Rayleigh Scattering: A Spectroscopic Tool for Nonlinear Optical Property Characterization, Charge Transfer Symmetry Investigation, and Nanoscale Interface Interrogation*. In *The Spectrum*, Bowling Green State University, Summer **2000**.

C. L. Haynes, R. P. Van Duyne, *Raman Spectroscopy*, in **Encyclopedia of Physical Science and Technology**, Third Edition, A. J. Bard, Ed., San Diego, Academic Press, 2001, 845 - 866.

G.C. Schatz and R.P. Van Duyne, *Electromagnetic mechanism of surface enhanced spectroscopy*, in **Handbook of Vibrational Spectroscopy**, J. M. Chalmers and P. R. Griffiths (Eds), John Wiley & Sons, Ltd, Volume 1, pp. 759-774 (2002).

K. Lance Kelly, Traci R. Jensen, Anne A. Lazarides and George C. Schatz, *Modeling Nanoparticle Optical Properties*, in **Metal Nanoparticles: Synthesis, Characterization and Applications**, D. Feldheim and C. Foss, Eds. Marcel-Dekker, New York, 2002,89-118.

C. Papers presented at meetings

A. K. Williams and J. T. Hupp, *Solution and Gas Phase Sensing of Alcohols and Aldehydes: Applications of a Sol-Gel Encapsulated Enzyme System*, American Chemical Society, Division of Polymeric Materials: Science and Engineering Preprints, 1998, **78**, 195-196.

C. L. Haynes, A. J. Haes, R. P. Van Duyne, Nanosphere Lithography: Synthesis and Application of Nanoparticles with Inherently Anisotropic Structures and Surface Chemistry, *Mat. Res. Soc. Symp. Proc.*, **635**, C6.3/1-C6.3/6 (2001).

A. J. Haes, C. L. Haynes, R. P. Van Duyne, Nanosphere Lithography: Self-assembled Photonic and Magnetic Materials, *Mat. Res. Soc. Symp. Proc.*, **636**, D4.8/1-D4.8/6 (2001).

A. A. Lazarides, K. L. Kelly and G. C. Schatz, Effective Medium Theory of DNA-linked Gold Nanoparticle Aggregates: Effect of Aggregate Shape, *Mat. Res. Soc. Symp. Proc.* **635**, C6.5.1-10 (2001).

Wang, Z. L.; Gao, R. P.; Poncharal, P.; de Heer, W. A.; Dai, Z. R.; Pan, Z. W. *Mechanical and electrostatic properties of carbon nanotubes and nanowires*. Materials Science & Engineering, C: Biomimetic and Supramolecular Systems, *Mat. Res. Soc. Symp. Proc.* (2001), C16(1-2), 3-10.

A. J. Haes, R. P. Van Duyne, "A Highly Sensitive and Selective Surface-Enhanced Nanobiosensor", *Mat. Res. Soc. Symp. Proc.*, **723**, O3.1.1 - O3.1.6 (2002).

C. L. Haynes, R. P. Van Duyne, "Plasmon Scanned Surface-Enhanced Raman Scattering Excitation Profiles", *Mat. Res. Soc. Symp. Proc.*, **728**, S10.7.1-S10.7.6 (2002).

D. Manuscripts submitted.

C. L. Haynes, R. P. Van Duyne, "Plasmon Scanned Surface-Enhanced Raman Excitation Spectroscopy", *J. Phys. Chem. B*, submitted December 17, 2002 (2003).

C. L. Haynes, A. D. McFarland, L. Zhao, R. P. Van Duyne, G. C. Schatz, L. Gunnarsson, J. Prikulis, B. Kasemo, M. Käll, "Nanoparticle Optics: The Importance of Radiative Dipole Coupling in Two-Dimensional Nanoparticle Arrays", *J. Phys. Chem. B*, submitted January 29 (2003).

K. Mitchell, F. Q. Huang, A. D. McFarland, C. L. Haynes, R. C. Somers, R. P. Van Duyne, J. A. Ibers, "The CsLnMSe₃ Semiconductors (Ln = Rare-Earth Element, Y; M = Zn, Cd, Hg)", *Inorg. Chem.*, submitted December 23, 2002 (2002).

F. Q. Huang, R. C. Somers, A. D. McFarland, R. P. Van Duyne, J. A. Ibers, "Syntheses, Structures, Optical Properties, and Theoretical Calculations of Cs₂Bi₂Zn₅, Cs₂Bi₂Cd₅, and Cs₂Bi₂Mn₅", *Journal of Solid State Chemistry*, submitted December 19, 2002 (2002).

I. Ijjaali, C. L. Haynes, A. D. McFarland, R. P. Van Duyne, J. A. Ibers, "Synthesis, Structure, and Optical Properties of the New LanthanumCopper Oxysulfide $\text{La}_3\text{CuO}_2\text{S}_3$ ", *Journal of Solid State Chemistry*, submitted December 14, 2002 (2002).

Strain Splitting of 1s Yellow Orthoexciton of Epitaxial Orthorhombic Cuprous Oxide Films on MgO [110], Y. Sun, Kiril Rivkin, J. Chen, and J. B. Ketterson P. Markworth, and R. P. Chang (submitted).

Numerical Studies of Second Harmonic Generation, K. Rivkin, A. Kryukov and J. B. Ketterson (submitted)

Ultra fast frequency selective optical switch based on a thin organic chromophoric film with a large second order nonlinear response, Gang Wang, Peiwang Zhu, Tobin J. Marks, and J. B. Ketterson. (submitted)

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Stefan Frank-postdoc

Z.L. Wang, Professor of Materials Science GIT

Philippe Poncharal, Postdoc (until 8/1/99) now Professor of Physics, Montpellier, France

Patrice Keghelian, Postdoc

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Ramiro Moro , grad student

Robert Nitsche, Undergraduate Exchange student (until 8/1/99)

Ken Dickerson, Undergraduate student, currently grad student at UCSD.

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Keith Stevenson-postdoc

Amy K. Williams-student*

Buford Lemon-student

Robert Williams-student

Jiang-tien Li - graduate student+

Robert Johnston - graduate student*

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E. Mirkin group

James J. Storhoff-student*
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Dr. John Krebs-postdoc
Dr. Andy Reynolds, NIH Postdoctoral fellowship
Dr. Andy (Thomas) Taton-postdoc
Dr. Gregory Mitchell-postdoc
Felicia Dixon (GE Minority Fellowship)-student
Keith Watson (NSERC Fellowship)-student*
Dr. Seunghun Hong-postdoc
Robert C. Mucic-student
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Zhi Li- graduate student
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Adam McFarland - graduate Student

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Honors, Awards, Degrees

Dr. Chad A. Mirkin –

Promoted to Charles E. and Emma H. Morrison Professor of Chemistry

BFGoodrich Collegiate Inventors Award 1998

Wilson Prize 1998(Harvard University; for the most outstanding chemist under the age of 40)

1999 ACS Award in Pure Chemistry and 1999 MRS Outstanding Young Investigator Award,
1998 PLU Fresenius Award

Mirkin's manuscript, "One Pot Colorimetric Differentiation of Polynucleotides with Single Base Imperfections Using Gold Nanoparticle Probes" entered the Top 10 List for most cited papers in Chemistry for 1998.

Discover 2000 Award for Technological Innovation, Elected Fellow of the American Association for the Advancement of Science, promoted to George B. Rathmann Professor of Chemistry.

2001 Leo Hendrick Baekeland Award (NU, 2001)

Crain's Chicago Business "40 under 40 Award" (NU, 2001)

Discover 2000 Award for Technological Innovation (NU, 2000)

Elected Fellow of the American Association for the Advancement of Science (NU, 2000)

I-Street Magazine's Top 5 List for Leading Academics in Technology (NU,2000)

Mark Ratner –

elected to American Academy of Arts and Science; Feynmann Prize(2001)

elected to National Academy of Science (2002)

George Schatz –

elected to International Academy of Quantum Molecular Science (2001)

elected to American Academy of Arts and Science (2002)

Morrison Professorship (2002)

James J. Storhoff (Mirkin): BFGoodrich Collegiate Inventors Award

Robert C. Mucic (Mirkin) won the NU Outstanding Thesis Award for his dissertation entitled: “Synthetically Programmable Nanoparticle Assembly using DNA”.

<u>Christy L. Haynes (Van Duyne),</u>	2001-2002 ACS Analytical Division Fellowship 2002-2003 NU Presidents Fellowship MRS Graduate Student Gold Award Spring 2002
<u>Amanda J. Haes (Van Duyne)</u>	2002-2003 NU NSEC Fellowship 2001-2002 ACS Analytical Division Summer Fellowship MRS Graduate Student Silver Award Spring 2002
<u>Xiaoyu Zhang (Van Duyne)</u>	2002-2003 NU MRSEC Fellowship

Ph.D. degrees:

Amy K. Williams, October, 1998. (Advisor: J. T. Hupp)

Thesis title: Fluorescence Studies of Dehydrogenases encapsulated in Silicate Matrices.
Placement: Senior Scientist, Air Products.

Grant T. Kiehne, September, 1999 (Advisor: J. B. Ketterson)

Thesis Title: Studies of Optical Second-Harmonic Generation in Single- and Multi-Layer Films Based on AlN
Placement: JDS Uniphase

Traci Jensen, September, 1999 (Advisors: G. C. Schatz, R. P. Van Duyne)

Thesis Title: Optical Characterization of Nanofabricated Silver Films: Surface Plasmon Resonance and Surface Enhanced Spectroscopy
Placement: Omega Optical

Robert C. Mucic, June 1999 (Advisor: C. A. Mirkin)

Thesis Title: “Synthetically Programmable Nanoparticle Assembly using DNA”.
Placement: Clinical Microsensors

Alex Shvartsburg, September 1999 (Advisor: M. F. Jarrold)

Thesis Title: Structural Characterization of Group 4 Element Clusters
Placement: Postdoc at York University/PE Sciex

Greg Rechtsteiner, November 2000, PhD (Advisors: M. Jarrold, R.P. Van Duyne)

Thesis Title: Experimental and Theoretical Studies of Hydrogen Terminated Silicon and Bare Carbon Clusters
Placement: Intel

Anton Kryukov, March 2000 (Advisor J. Ketterson)

Thesis title: Surface plasmon near-field optical microscopy and second harmonic generation in multilayer structures
Placement:

Michelle Duval Malinsky, December, 2000 (Advisor: R.P. Van Duyne)

Thesis Title: Localized Surface Plasmon Resonance Spectroscopy of Silver Nanoparticles and Raman Spectroscopy Using Liquid-Core Optical Fibers: Fundamentals and Applications
Placement: Senior Chemist, 3M Environmental Laboratory

Matthew T. Smith, December, 1999 (Advisors: M. A. Ratner, R.P. Van Duyne)

Thesis Title: Nanosphere Lithography: Angle Resolved Deposition, Magnetic

Nanoparticles, and the Scanning Probe Raman Microscope
 Placement: Research Chemist, Union Carbide Corporation
 Anjeanette D. Ormonde, Ph.D. Chemistry, December 2001 (R.P. Van Duyne)
 Thesis – "Nanosphere Lithography: I. Fabrication and Characterization of Large Area Silver Nanoparticle Arrays. II. Electrochemical Tuning of Silver Nanoparticle Size. III. Nanoparticle Shape As A Function of Size for Ag, Au, Co, Pd, and Pt Nanoparticles"
 Placement – Unilever HPC-USA, Rolling Meadows, IL
 K. Lance Kelly, Ph. D. Chemistry, January 2002 (G. C. Schatz, R. P. Van Duyne)
 Thesis – "Classical Electrodynamics of Surface Enhancing Nanoparticles"
 Placement – Postdoc, Yale University
 Guosheng Wu, Ph. D. Chemistry, December 2001 (G. C. Schatz)
 Thesis – "Theory of DNA Melting"
 Placement – Eli Lilly Corp.
 Robert C. Johnson, Ph. D. Chemistry, 2002 (J. T. Hupp)
 Thesis - "Linear and Nonlinear Optical Properties of Metal Nanoparticles and Nanoparticles Assemblies"
 James Snyder, Ph.D. Chemistry (2002) (M. A. Ratner, D. F. Shriver)
 Thesis – Ion Transport in Polyelectrolytes
 Placement - ARL

(8). Inventions

NU22073	Surface-enhanced Raman Nanobiosensor
NU22078	A Nanoscale Optical Biosensor for Immunoassay

(9) Bibliography-none

(10) Appendices

Appendix 1. Technology Transfer

Mirkin worked closely with Dr. Michael Goode (Edgewood, MD) to evaluate the utility of our DNA detection systems for military use. Joint field trials were completed at Dugway Air Force Base in late March. These studies allowed us to compare and contrast our detection system with others from within the military and private companies. Joining us at Dugway were scientists from Nanosphere, Inc., the start-up company attempting to commercialize the technology.

Hupp worked with ChemMotif, a small startup company in Concord, MA, on development and commercialization of the nanoparticle based technology for ultrasensitive heavy-metal detection invented by Hupp and coworkers.

Jarrold provided mobility software to Tom Evans at Dugway

Ratner worked with EIC Laboratories, including a collaborative DoD-SBIR on Optical Properties of Tuned Molecular Media (with Phase II, EIC Labs in Norwood, MA)
The aim of this effort is development of tunable, nonlinear molecular chromophores both for imaging interactions and for laser hardening applications.

Ratner had active interactions with scientists at NRL, including a molecular electronics project with R. Shashidar.

Ratner continues as a member of the technical advisory board of the Dow Chemical Company; Dow is involved in rather extensive licensing and development of light emitting diode structures based on the optoelectronic properties of substitutive fluorenes; Ratner has acted as a consultant on this project.

Ratner visited ARL to discuss molecular electronics modeling (with C. Chabylowski and S. Karna)

Schatz began collaborating with scientists from Integrated DNA Technologies, Inc. concerning the modeling of oligonucleotide melting.

Van Duyne did collaborative research on surface-enhanced Raman spectroscopy with Dr. Nick Fell at the Army Research Laboratories Adelphi. This work has involved the delivery of SERS-active surfaces fabricated by nanosphere lithography at Northwestern to ARL. Dr. Fell and his postdoctoral associate visited Northwestern January 23-25, 2002 to learn NSL first hand. A return visit is scheduled for winter 2003.

Appendix 2: Outreach

1. Communication

The MURI web page is located at: <http://www.chem.nwu.edu/~muri>. This page gives a general summary of research activities and personnel, along with more detailed descriptions that are contained in the Annual Reports. In addition, it includes abstracts of talks given in the MURI kick-off meetings, and in MURI group meetings.

2. Summer minority research program

We ran a minority summer research program for five years. Five students participated in the program, one each summer.

3. MURI Group meetings at Northwestern

All of the research groups in the program have their own research group meetings. In addition to this we held monthly group meetings of all the groups at Northwestern. This group meeting continues to operate even though the grant is over.

4. MURI outside speakers

In addition to the MURI group meetings, we also held MURI seminars (typically one each month, as well as joint activities with other seminar programs) in which outside speakers with interests that overlap with our research programs are brought in to spend one or more days.

5. MURI review meeting (Northwestern University)

Review meetings were held each year of the grant.